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Selective Co-oligomerization of Ethylene and Styrenes by Half-Titanocene Catalysts and Synthesis of Polyethylenes with 4-Aryl-1-butyl Branches

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ABSTRACT: Copolymerization of ethylene and styrene with the catalytic system $Cp^{*}TiMe_3-B(C_6F_5)_3$ under suitable conditions affords a new polymer having a polyethylenic backbone with 4-phenyl-1-butyl branches as the main solid product. Analysis of the polymerization mixtures evidences the formation of significant amounts of unsaturated ethylene−styrene co-oligomers. A detailed characterization of the oligomeric fraction by GC-MS and NMR analysis suggests some selectivity of the co-oligomerization, i.e., the prevailing formation of phenylhexenes and the absence of phenylbutenes. These unexpected results have been ascribed to the multisite nature of the catalytic system, containing a species able to co-oligomerize ethylene and styrene to phenylhexenes and another species able to copolymerize the formed 6-phenyl-1-hexene with ethylene. A mechanism involving Ti(II) active species and metallacycle intermediates has been proposed to explain the observed selectivity in the co-oligomerization, by analogy with the mechanism proposed for the selective trimerization of ethylene to 1-hexene by the same catalyst. Extension of this study to catalysts based on other half-titanocenes activated by methylalumoxane results in similar findings; optimization of the reaction conditions for the $CpTiCl_3$−MAO catalyst results in styrene conversions to unsaturated co-oligomers >90%. Dual-catalyst systems, with one component co-oligomerizing ethylene and styrene and the other copolymerizing the formed 6-phenyl-1-hexene with ethylene, have been used to selectively produce polyethylenes with 4-phenyl-1-butyl branches. Use of substituted styrenes, i.e., *p*-methylstyrene, *p*-*tert*-butylstyrene, *p*-chlorostyrene, and *m*-methylstyrene, as the comonomers results in the formation of polyethylenes having the corresponding 4-aryl-1-butyl branches as well as oligomeric fractions analogous to those obtained from styrene.

Introduction

The copolymerization of ethylene (E) and styrene (S) is a rather recent achievement, following the development of the homogeneous catalysts based on cyclopentadienyl derivatives of group 4 metals and methylaluminoxane (MAO).[1] Our interest in E−S copolymerization originated from the studies of the catalytic systems active in the syndiotactic-specific polymerization of styrene.[2] These catalysts are based on a variety of soluble titanium compounds in different oxidation states, the most efficient being those based on monocyclopentadienyl derivatives, such as $CpTiCl_3$, and an activator, typically MAO. In an early work[3] from our laboratory the latter catalyst was tested in E−S copolymerization, affording, under suitable conditions, novel E−S copolymers containing up to 35 mol % styrene, in a mixture with variable amounts of homopolymers, depending on the reaction conditions and especially the MAO/Ti ratio. The latter finding was tentatively explained by hypothesizing that the reaction between $CpTiCl_3$ and MAO affords different active species promoting respectively either homopolymerization or copolymerization of the two monomers. The E−S copolymers were characterized by ^{13}C NMR spectroscopy, indicating the presence of EEE, EES, ESE, and SES sequences, while no regioregular SS sequences were detected. This finding suggested that the catalytic species affording the E−S copolymer is not capable of homopolymerizing styrene.[3]

At about the same time, Kakugo et al.[4] reported that a catalyst based on 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxy)titanium dichloride and methylalumoxane was able to produce, with low activity and under rather extreme conditions, a substantially alternating E−S copolymer, in a mixture with syndiotactic polystyrene (s-PS). A more recent study on various bridged bis(phenolate)titanium catalysts by Mülhaupt et al.[5] confirmed the production of E−S copolymers with this class of catalysts, although these authors did not obtain alternating ethylene−styrene copolymers, even when using the Kakugo's catalyst. Subsequently, a patent by Stevens et al.[6] disclosed novel catalysts based on monocyclopentadienyl titanium or zirconium complexes with an amido ligand covalently attached to the Cp ring ("constrained-geometry" catalysts) that efficiently copolymerize ethylene with α-olefins and styrene. The E−S copolymers obtained with these catalysts were defined "pseudorandom", meaning they do not contain any regioregularly arranged SS sequences, even at styrene contents approaching 50 mol %. While the copolymer structure is very similar to that of the copolymer produced with the above-mentioned simple $CpTiCl_3$ catalyst,[3] the most relevant advance is the fact that these bridged Cp-amido catalysts are truly "single site", and thus homogeneous E−S copolymers, free of homopolymers, can be obtained.

Many other catalytic systems have subsequently been investigated for the copolymerization of ethylene and

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Table 1. Ethylene−Styrene Copolymerizations with $Cp^*TiMe_3-B(C_6F_5)_3$ [a]

run	styrene (mL)	temp (°C)	oligomeric fraction (g)	solid polymer (g)
1	4	0	0.4	0.7
2	2.5	20	0.3	1.3
3[b]	2.5	20	0.35	0.4
4[c]	2.5	20	0.1	0.5
5[d]	2.5	20		*e*
6	3	50	0.25	0.9
7	3.5	75	0.1	0.8

[a] Polymerization conditions: $Cp^*TiMe_3 = B(C_6F_5)_3 = 88$ μmol; $AlMe_3 = 0.1$ mmol; toluene + styrene = 26 mL; ethylene = 1 atm; time = 20 min. [b] Only 44 μmol of $B(C_6F_5)_3$ was used. [c] No $AlMe_3$ was added. [d] Conditions such as in run 2, but no Cp^*TiMe_3 was present. [e] Traces.

styrene, including the typical *ansa*-metallocene catalysts widely used for the polymerization of α-olefins.[7] Proper selection of the catalyst structure and of the polymerization conditions has allowed the synthesis of E−S copolymers of different compositions and structures, ranging from crystalline thermoplastics to elastomeric products, such as stereoregular isotactic poly(ethylene-*alt*-styrene)[8] and E−S "Bernoullian" copolymers, i.e., containing also some regioregular SS sequences.[9] In this context, we have previously reported[10] that the MAO-free catalyst $Cp^*Ti(CH_2Ph)_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$)−$B(C_6F_5)_3$ affords an atactic poly(ethylene-*alt*-styrene), even at low S/E feed ratio, in mixture with some homopolymers.

More recently, extension of this study to the related catalyst $Cp^*TiMe_3-B(C_6F_5)_3$ has resulted in unexpectedly different findings, i.e., the prevailing production of polyethylenes with variable amounts of 4-phenyl-1-butyl branches.[11] In this paper, we report a GC-MS and NMR study on this copolymerization system, evidencing the formation of significant amounts of unsaturated E−S co-oligomers, including 6-phenyl-1-hexene among the main components. Full characterization of the oligomeric fraction indicates some selectivity in the co-oligomerization, for which a mechanism involving metallacycle intermediates is proposed. Extension of this investigation to $Cp'TiCl_3$−MAO (Cp' = cyclopentadienyl, pentamethylcyclopentadienyl, indenyl) catalysts, as well as to other vinyl−aromatic comonomers (*p*-methylstyrene, *m*-methylstyrene, *p*-*tert*-butylstyrene, *p*-chlorostyrene), is also reported.

Results

E−S Co-oligomerization with $Cp^*TiMe_3-B(C_6F_5)_3$ and Characterization of the Oligomers. Several ethylene−styrene copolymerization runs were carried out in the presence of the catalytic system $Cp^*TiMe_3-B(C_6F_5)_3$ under variable conditions (see Table 1). As a general procedure, the copolymerizations were quenched by pouring the reaction mixture in acidified methanol, and the precipitated polymers were separated by filtration. The raw polymers consist of a mixture of macromolecules, which can be fractionated and analyzed as previously reported.[11] Under suitable conditions, the main solid product is a polyethylene containing 3−5 mol % 4-phenyl-1-butyl branches, contaminated by some alternating E−S copolymer and some homopolymers.[11] To elucidate the origin of the phenylbutyl-branched PE, the soluble parts of the copolymerization mixtures were shaken with water and heptane, and then the organic layers were separated and treated as described in the Experimental Section, affording liquid oligomeric fractions, which were analyzed by ^1H NMR: the spectra (see e.g. Figure 1) indicated the presence of several aromatic olefins. GC analysis showed the presence of three major products (see Figure 2, peaks A, B, D) plus some minor ones (peaks C and E). GC-MS analysis gave MW = 160 for peaks A, B, and C and MW = 188 for peaks D and E. The mass spectra are consistent with the presence of three oligomers of formula $C_{12}H_{16}$ (A, B, C) and two of formula $C_{14}H_{20}$ (D, E).

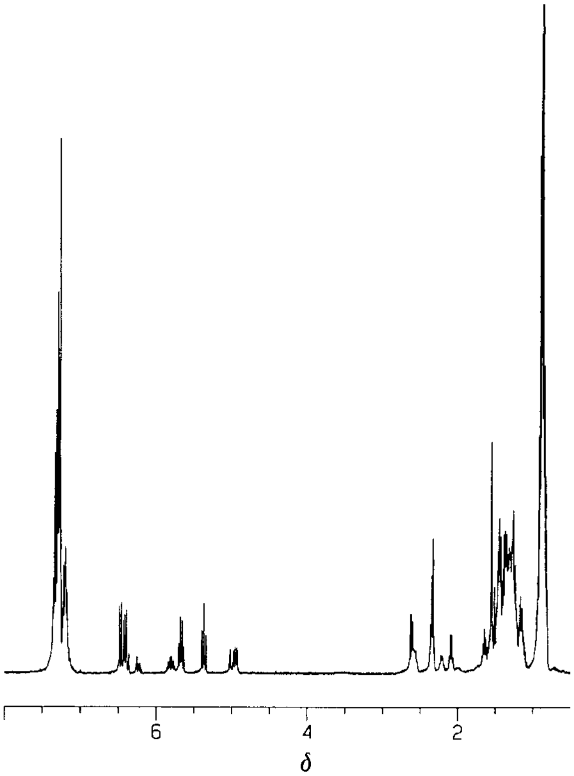


Figure 1. ^1H NMR ($CDCl_3$, 25 °C) spectrum of the oligomeric fraction obtained in run 1.

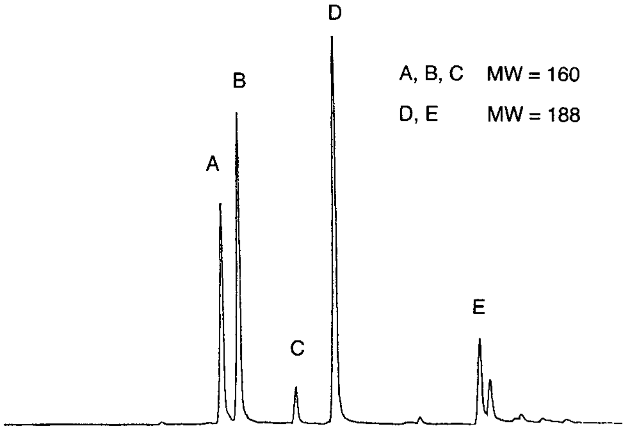


Figure 2. Gas chromatogram of the oligomeric fraction obtained in run 1.

The ^{13}C NMR spectra of the oligomeric fractions are rather complex (see e.g. Figure 3), owing to the presence of several compounds. To simplify the spectrum, the oligomeric fraction obtained in run 1 was hydrogenated with H_2/Pd on activated charcoal. As expected, the ^{13}C NMR spectrum (Figure 4) indicates that the three $C_{12}H_{16}$ isomers were converted in only one $C_{12}H_{18}$ compound, which was identified as 1-phenylhexane; the major $C_{14}H_{20}$ isomer was converted in the saturated

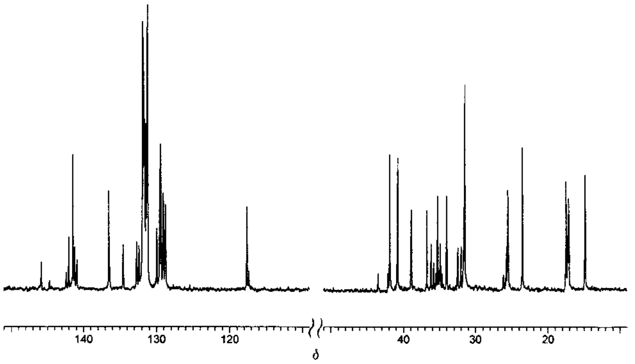


Figure 3. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of the oligomeric fraction obtained in run 1 (see Table 2 for resonance assignment).

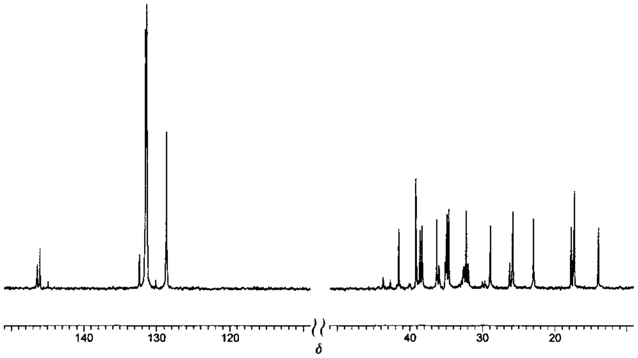


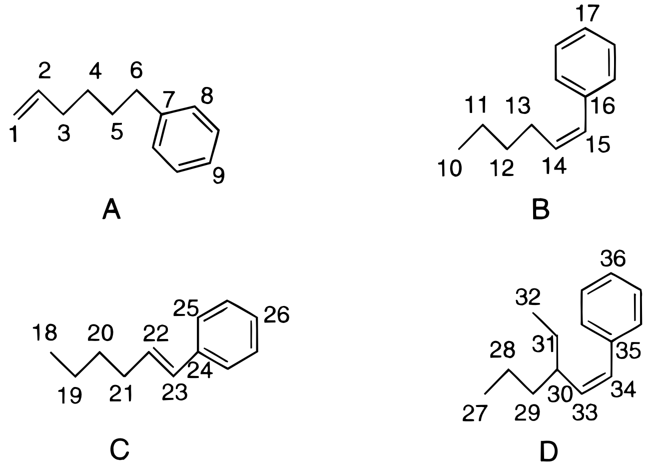
Figure 4. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of the oligomeric fraction obtained in run 1 after hydrogenation.

Table 2. ^{13}C NMR Data of the Main Ethylene−Styrene Co-oligomers[a]

δ (ppm from TMS)	assignt, C	δ (ppm from TMS)	assignt, C
11.6	32	114.4	1
13.9	10	125.5	9
14.0	18	125.8	34
14.3	27	125.9	25
20.3	28	126.2	15
22.3	11, 19	126.4	17
28.3	13, 31	126.8	26
28.4	4	128.2	8
30.8	5	129.5	23
31.5	20	131.2	22
32.0	12	133.2	14
32.7	21	137.5	16
33.5	3	137.8	24
35.7	6	137.9	35
37.6	29	138.2	33
38.6	30	138.8	2
		142.6	7

[a] The resonances are assigned according to Scheme 1.

Scheme 1. Structures of the Main Ethylene−Styrene Co-oligomers



$C_{14}H_{22}$ hydrocarbon, identified, with the aid of chemical shifts increments and DEPT experiments, as 1-phenyl-3-ethylhexane. Comparison with literature data, DEPT, and 2-D experiments, as well as comparison with NMR spectra of oligomeric fractions obtained in runs performed under different conditions and thus having different compositions (see below), allowed us to establish the structure of the main oligomers. The two major $C_{12}H_{16}$ isomers are identified as 6-phenyl-1-hexene (**A**) and *cis*-1-phenyl-1-hexene (**B**), while the minor $C_{12}H_{16}$ isomer is *trans*-1-phenyl-1-hexene (**C**). The third major component is a branched $C_{14}H_{20}$ isomer, namely 3-ethyl-1-phenyl-1-hexene (**D**), while the higher boiling $C_{14}H_{20}$ isomer (**E**) was identified as 1-phenyl-1-octene. See Scheme 1 and Table 2 for the structures and ^{13}C NMR data of compounds **A**−**D**.

Many other polymerization runs have been performed with the same catalyst under different conditions and the organic layers analyzed as described above. In all cases, the same oligomers were obtained, although in some cases in slightly different relative abundance. It is worth noting that the addition of some $AlMe_3$ to the polymerization mixture is beneficial for the production of both the oligomers and the solid polymer (cf. runs 2 and 4 in Table 1); however, the same oligomers are formed also in the absence of $AlMe_3$ (run 4), suggesting that Al is not essential for the generation of the active species promoting the co-oligomerization (see the Discussion section for further comments on this matter). In contrast, mixtures of $AlMe_3$ and $B(C_6F_5)_3$ under identical conditions (see run 5) do not produce the mentioned E−S co-oligomers, but only traces of atactic polystyrene.

E−S Co-oligomerization with MAO-Based Catalysts. To check whether the above unexpected results are peculiar to the $Cp^*TiMe_3−B(C_6F_5)_3$ catalytic system, we have tested different catalytic systems based on the half-titanocenes $CpTiCl_3$, Cp^*TiCl_3, and $(Ind)TiCl_3$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$, $Ind = \eta^5\text{-}C_9H_7$), activated by MAO, in the co-oligomerization of ethylene and styrene. The main reaction conditions and results are summarized in Table 3. The reaction mixtures were worked up and analyzed as described above. All of the investigated catalysts produced significant amounts of unsaturated co-oligomers, having essentially the same structures found above. However, some significant differences can be appreciated by comparing the GC traces and the ^{13}C NMR spectra, the most apparent involving the relative abundance of *cis*-1-phenyl-1-hexene (**B**) vs *trans*-1-phenyl-1-hexene (**C**): in fact, the fraction of the cis isomer, which is largely prevailing for the $Cp^*TiMe_3−B(C_6F_5)_3$ catalyst, decreases moving to Cp^*TiCl_3−MAO and becomes negligible for $CpTiCl_3$−MAO and $(Ind)TiCl_3$−MAO (see Figures 5−7). Also, the last two catalysts do not produce the branched $C_{14}H_{20}$ isomer (**D**), but two linear ones, i.e., the already found 1-phenyl-1-octene (**E**) and the previously undetected α-olefin 6-phenyl-1-octene (**F**), although in the case of $(Ind)TiCl_3$−MAO these are much less abundant than the (phenyl)hexenes **A** and **C**. It is also worth noting that $CpTiCl_3$−MAO and, to a lesser extent, $(Ind)TiCl_3$−MAO are highly selective co-oligomerization catalysts: e.g. in run 8 about 1 g of oligomers was produced in 20 min at

Table 3. Ethylene−Styrene Copolymerizations with $Cp'TiCl_3$−MAO[a]

run	catalyst (μmol)	MAO, mmol	styrene, mL	*T*, °C	time, min	oligomeric fraction, g	solid polymer, g
7	Cp^*TiCl_3 (88)	6.0	2.5	20	20	0.15	traces
8	$CpTiCl_3$ (88)	6.0	2.5	20	20	1.0	traces
9	$(Ind)TiCl_3$ (88)	6.0	2.5	20	20	0.5	0.1
10	Cp^*TiCl_3 (52)	4.0	2.0	50	30	0.3	0.1
11	$CpTiCl_3$ (80)	5.2	0.5	20	20	0.5	traces
12	$CpTiCl_3$ (80)	5.2	2.5	20	20	1.3	traces
13	$CpTiCl_3$ (80)	5.2	5	20	20	1.6	traces
14	$CpTiCl_3$ (80)	5.2	2.5	20	40	2.4	0.2
15	$CpTiCl_3$ (80)	5.2	2.5	20	60	2.7	0.3
16	$CpTiCl_3$ (80)	5.2	2.5	20	120	2.8	0.35
17	$CpTiCl_3$ (80)	5.2	1.0	20	40	1.3	0.2
18	$CpTiCl_3$ (80)	2.6	2.5	20	20	0.3	traces
19	$CpTiCl_3$ (80)	10.4	2.5	20	20	1.7	0.1
20	$CpTiCl_3$ (80)	5.2	2.5	0	20	0.2	traces
21	$CpTiCl_3$ (80)	5.2	2.5	40	20	1.1	0.2
22	$CpTiCl_3$ (80)	5.2	2.5	60	20	0.6	0.4

[a] $Cp' = \eta^5\text{-}C_5H_5$ (Cp); $\eta^5\text{-}C_5Me_5$ (Cp*); $\eta^5\text{-}C_9H_7$ (Ind). Polymerization conditions: toluene + styrene = 26 mL; ethylene = 1 atm.

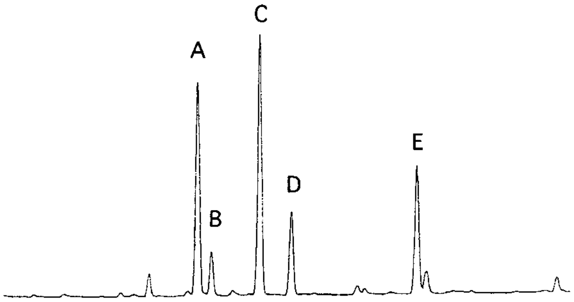


Figure 5. Gas chromatogram of the oligomeric fraction obtained in run 7 (see Table 3). See Scheme 1 for peak assignment.

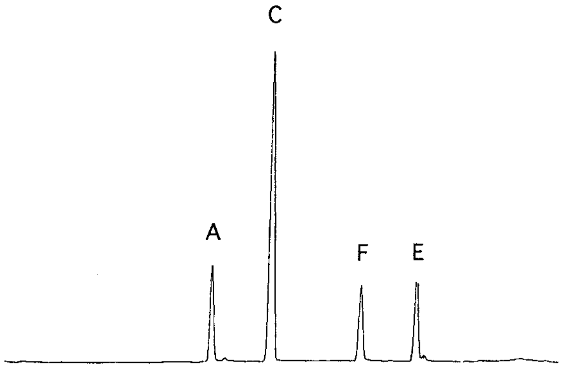


Figure 6. Gas chromatogram of the oligomeric fraction obtained in run 8 (see Table 3). See Scheme 1 for peak assignment.

20 °C (vs <0.05 g of solid polymer) with a ~30% conversion of styrene. On the basis of these findings, an optimization of the co-oligomerization was attempted, investigating the effects of various parameters, i.e., the concentration of styrene, the reaction time, the amount of MAO, and the temperature, on the performances of the catalyst $CpTiCl_3$−MAO (see Table 3). Analysis of the data indicates that (i) increasing the styrene/ethylene ratio in the feed leads to an increase of the yield of co-oligomers, but the conversion of styrene decreases rapidly (runs 11−13); (ii) the yield of co-oligomers increases with reaction time up to ~1 h, although more polymer (consisting mainly of phenylbutyl-branched PE) is produced at longer times (runs 14−16); (iii) the yield of co-oligomers increases with increasing MAO/Ti molar ratio up to 120 (runs 12, 18, 19), while higher ratios tend to favor polymerization; (iv) the yield of co-oligomers reaches a maximum at 20 °C and decreases at higher temperatures, which favor polymerization (runs 12, 20−22). Proper choice of the conditions results in conversions of styrene to E−S co-oligomers >90% (run 17).

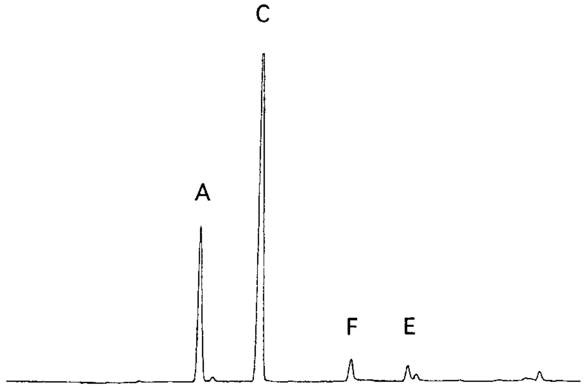


Figure 7. Gas chromatogram of the oligomeric fraction obtained in run 9 (see Table 3). See Scheme 1 for peak assignment.

Use of Dual-Catalyst Systems for the Selective Production of Polyethylene with 4-Phenyl-1-butyl Branches. As previously reported,[11] a polyethylene with 4-phenyl-1-butyl branches is obtained from an E−S feed with the $Cp^*TiMe_3−B(C_6F_5)_3$ catalyst. This unexpected result was ascribed to the multisite nature of the catalytic system, containing a species able to co-oligomerize ethylene and styrene to 6-phenyl-1-hexene and another species able to copolymerize the latter with ethylene. However, owing to the presence of different active species, the phenylbutyl-branched PE was invariably produced in a mixture with an alternating E−S copolymer and some homopolymers (PE and s-PS). To produce the phenylbutyl-branched PE selectively, we explored the use of a dual-catalyst system,[12] with one component producing the unsaturated oligomers and the second one copolymerizing the formed α-olefin(s) with ethylene. $CpTiCl_3$ was selected as the co-oligomerization catalyst on the basis of the above-reported results. Two zirconocenes, Cp_2ZrCl_2 and *rac*-$Et(Ind)_2ZrCl_2$, and two "low-valency" catalysts,[13] $[(C_5Me_4)(CH_2)_2NMe_2]TiCl_2$ and $[(C_5Me_4)(CH_2)_2NBu_2]TiCl_2$, all activated by MAO, were tested as copolymerization catalysts using the preisolated oligomer mixtures produced in runs 12−15 as the comonomer. In any case the obtained polymers consist of polyethylene with variable amounts of 4-phenyl-1-butyl branches, ranging between 1 and 5 mol % (evaluated from ^{13}C NMR), the two "low-valency" catalysts being the most efficient in the incorporation of 6-phenyl-1-hexene (see Table 4).

Subsequently, several two-step runs were carried out: an ethylene−styrene co-oligomerization step was performed with $CpTiCl_3$−MAO under the above optimized conditions, followed by the addition of the second catalyst for the copolymerization step. Some representative data are reported in Table 4: under suitable conditions, the target phenylbutyl-branched PE is selectively produced for all the tested dual-component catalysts, with the two "low-valency" catalysts providing the highest comonomer incorporation (see e.g. the ^{13}C NMR spectrum displayed in Figure 8). The main problem for the two-step procedure seems to be the presence of residual styrene, which slows down the

Table 4. Production of 4-Phenyl-1-butyl-Branched PE with Dual-Catalyst Systems

run	catalyst	solid polymer, g	branches,[a] mol %
23[b]	Cp_2ZrCl_2	1.3	1
24[b]	*rac*-$Et(Ind)_2ZrCl_2$	1.2	2
25[b]	$Cp^*(CH_2)_2NMe_2TiCl_2$	0.7	4.5
26[b]	$Cp^*(CH_2)_2NBu_2TiCl_2$	0.5	5
27[c]	$CpTiCl_3-Cp_2ZrCl_2$	0.9	1
28[c]	$CpTiCl_3$-*rac*-$Et(Ind)_2ZrCl_2$	1.4	3
29[c]	$CpTiCl_3-Cp^*(CH_2)_2NMe_2TiCl_2$	0.5	6
30[c]	$CpTiCl_3-Cp^*(CH_2)_2NBu_2TiCl_2$	0.6	6

[a] Evaluated from ^{13}C NMR. [b] Conditions: toluene = 23 mL; catalyst = 10 μmol; MAO = 8.6 mmol; ethylene = 1 atm; comonomer = 1.2 g of the oligomeric mixture resulting from runs 12−15; temperature = 55 °C; time = 15 min. [c] Conditions: first step: toluene = 25 mL; $CpTiCl_3$ = 80 μmol; MAO = 5.2 mmol; ethylene = 1 atm; styrene = 1.0 mL; temperature = 20 °C; time = 40 min; in the second step, to the reaction mixture was added: second metal complex = 10 μmol; MAO = 3.4 mmol; temperature = 80 °C; time 15 min.

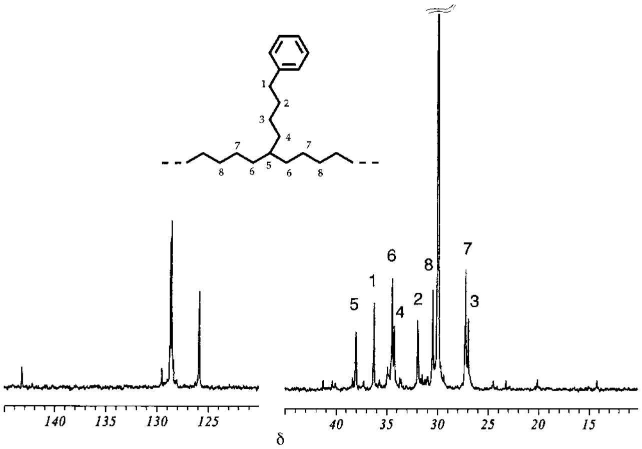


Figure 8. ^{13}C NMR ($C_2D_2Cl_4$, 120 °C) spectrum of a polyethylene with 4-phenyl-1-butyl branches produced by a dual-catalyst system (run 30 of Table 4). Resonances are assigned according to the scheme of the figure.

Table 5. Copolymerizations of Ethylene and Substituted Styrenes with $Cp^*TiMe_3-B(C_6F_5)_3$ [a]

run	comonomer (mL)	solid polymer, g	oligomeric fraction, g
31	*p*-methylstyrene (2.5)	1.2	0.35
32	*m*-methylstyrene (2.9)	0.45	0.5
33	*p-tert*-butylstyrene (2.5)	1.0	0.15
34	*p*-chlorostyrene (2.6)	0.65	0.15

[a] Polymerization conditions: $Cp^*TiMe_3 = B(C_6F_5)_3 = 80$ μmol; $AlMe_3$ = 0.1 mmol; toluene = 20 mL; ethylene = 1 atm; temperature = 20 °C; time = 15 min.

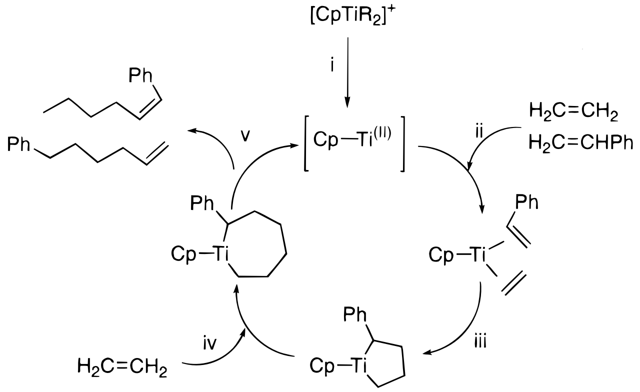
copolymerization step: as a matter of fact, phenylbutyl-branched PE's are produced only when most of styrene is consumed in the co-oligomerization step.

Co-oligomerization of Substituted Styrenes with Ethylene and Production of PE with 4-Aryl-1-butyl Branches. The above investigation was extended to some substituted styrenes, i.e., *p*-methylstyrene, *m*-methylstyrene, *p-tert*-butylstyrene, and *p*-chlorostyrene. Several copolymerizations of the mentioned styrenes with ethylene were performed using $Cp^*TiMe_3-B(C_6F_5)_3$ as the catalyst under conditions similar to those used to maximize the production of PE with 4-(phenyl)1-butyl branches.[11] The main reaction conditions and results are summarized in Table 5. The solid polymers obtained in runs 31−34 (samples 1−4) were analyzed by ^{13}C NMR, indicating in all cases the presence of a complex mixture of macromolecules, including the homopolymers and ethylene−substituted-styrene copolymers.[11] Thus, the raw polymers were extracted by stirring with THF at room temperature, and the THF-insoluble fractions were examined by ^{13}C NMR, showing that they mainly consist of polyethylenes with 4-aryl-1-butyl branches (aryl = *p*-tolyl, sample 1; *m*-tolyl, sample 2; *p-tert*-butylphenyl, sample 3; *p*-chlorophenyl, sample 4). The soluble parts of the copolymerization mixtures obtained in runs 31−34 (samples S1−S4) were worked up and analyzed as described above. GC and ^1H NMR analysis showed that the main components of oligomeric samples S1−S3 are the homologues of the olefins obtained from ethylene−styrene co-oligomerization with the same catalyst, i.e., 6-aryl-1-hexene, *cis*-1-aryl-1-hexene, and 1-(aryl)-3-ethyl-1-hexene (aryl = *p*-tolyl, sample S1; *m*-tolyl, sample S2; *p-tert*-butylphenyl, sample S3). In contrast, the main component of sample S4 is *trans*-1-*p*-chlorophenyl-1-hexene.

Discussion

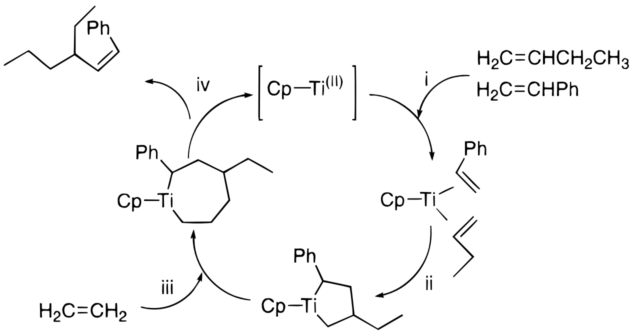
We first introduced $Cp^*TiMe_3-B(C_6F_5)_3$ as an efficient catalyst for the polymerization of olefins and for the syndiotactic-specific polymerization of styrene.[14] Subsequently, this catalyst has been extensively investigated[15] by several authors in the polymerization of olefins, cycloolefins, and styrene, occurring via a Ziegler−Natta mechanism, as well as in the polymerization of monomers such as vinyl ethers, *N*-vinylcarbazole, and isobutene, occurring via a carbocationic mechanism. The results reported in this paper further expand the scope of this versatile catalyst, which has been shown to convert an ethylene−styrene feed to such different products as PE, s-PS, poly(ethylene-*alt*-styrene), 4-phenyl-1-butyl-branched PE, and a variety of unsaturated E−S co-oligomers. These findings are reasonably related to a multisite nature of the catalyst. Actually, the catalytic system $Cp^*TiMe_3-B(C_6F_5)_3$ has been deeply investigated by NMR and ESR spectroscopy, indicating the formation of several organometallic species. In particular, the $[Cp^*TiMe_2]^+$ cationic complex, which is the primary reaction product,[15a] has been shown to decompose to species of lower oxidation state, including the Ti(III) $[Cp^*TiMe]^+$ complex.[16] Also, dimeric Me-bridged Ti complexes as well as Ti-μMe-B zwitterions have been detected.[17] Related MAO-activated half-sandwich catalysts have been also shown to be multisite systems, containing Ti(IV), Ti(III), and Ti(II) species.[18] Although the role of these different organometallic species in catalysis is still under debate,[2a,15d,18b] several lines of evidence point to the $[Cp^*Ti^{IV}R_2]^+$ cation as the true catalyst in the polymerization of olefins and to the $[Cp^*Ti^{III}R]^+$ cation as the true catalyst producing syndiotactic polystyrene. The production of phenylbutyl-branched PE could be ascribed as well to $[Cp^*Ti^{IV}R_2]^+$, which should efficiently copolymerize ethylene with 6-phenyl-1-hexene, owing to its open coordination sphere. On the other hand, the production of significant amounts of unsaturated E−S co-oligomers clearly involves a different active species, i.e., a complex unable to incorporate long ethylene or styrene sequences. Although no direct evidence on the structure of such complex is currently available, the structures of the obtained co-oligomers provide some mechanistic insight. As a matter of fact, the co-oligomerization reaction appears rather selective, affording mainly two trimers (containing two

Scheme 2. Mechanism for the Formation of Phenyl-1-hexenes[a]



[a] All of the titanium complexes in the catalytic cycle have a +1 overall charge.

Scheme 3. Mechanism for the Formation of 3-Ethyl-1-phenyl-1-hexene[a]



[a] All of the titanium complexes in the catalytic cycle have a +1 overall charge.

E and one S units), namely *cis*-1-phenyl-1-hexene and 6-phenyl-1-hexene, and one branched tetramer (containing three E and one S units), namely 3-ethyl-1-phenyl-1-hexene, while, e.g., no phenylbutenes are detected. The picture is similar for the other half-titanocene catalysts tested, with some minor (although interesting) differences, e.g., the preferential formation of *trans*-1-phenyl-1-hexene rather than the cis isomer. Concerning the origin of the oligomers, the most obvious mechanism would involve a sequence of insertion/β-H elimination steps: e.g., 6-phenyl-1-hexene would originate from primary styrene insertion into Ti−H bonds, followed by the insertion of two ethylene units and β-hydrogen elimination in the resulting $Ti-(CH_2)_6Ph$ species, while 1-phenyl-1-hexene would derive from the insertion of two ethylene molecules into Ti−H bonds followed by secondary styrene insertion and β-hydrogen elimination in the resulting $Ti-CH(Ph)(CH_2)_4CH_3$ species. However, several findings are not easily explained by this mechanism, i.e., (i) the observed selectivity in phenylhexene oligomers vs the absence of phenylbutene analogues; (ii) the insertion of styrene with opposite regiochemistries required to explain the formation of 6-phenyl-1-hexene and 1-phenyl-1-hexene; (iii) the significant production of the branched tetramer, 3-ethyl-1-phenyl-1-hexene, which cannot be justified by any simple sequence of insertions/eliminations. Moreover, in a related study[19] concerning the homopolymerization of ethylene by the same catalyst, we have recently observed the selective production of *n*-butyl-branched PE and 1-hexene, confirming the preference for olefin trimerization even in the absence of styrene. We have tentatively explained[19] the selective trimerization of ethylene to 1-hexene with a mechanism involving metallacycle intermediates, analogous to that previously proposed for homogeneous chromium catalysts.[20]

A similar mechanism could easily account for the selective formation of the major unsaturated E−S co-oligomers. The formation of phenyl-1-hexenes would involve (see Scheme 2) (i) reductive elimination in a $[Cp^*TiR_2]^+$ cation (R = hydrocarbyl or H) affording a cationic Ti(II) species, (ii) coordination of one styrene and one ethylene molecule to the latter, (iii) oxidative addition to form a cationic Ti(IV) Ph-substituted titanacyclopentane, (iv) further insertion of ethylene at the less hindered site yielding a 2-(phenyl)titanacycloheptane, which, in turn, (v) can undergo reductive elimination via β-H transfer either (a) from C3, yielding 1-phenyl-1-hexene, or (b) from C6, yielding 6-phenyl-1-hexene. The absence of appreciable amounts of 1-hexene under these conditions (at variance with what is observed in the presence of ethylene only[19]) could be justified by the preferential coordination of one styrene molecule (rather than two ethylene molecules, reasonably for electronic reasons) in step ii. The relative amounts of internal and terminal olefins, as well as the preferential formation of either *cis*- or *trans*-1-phenyl-1-hexene, would depend on the relative stabilities of the required transition states for β-H tranfer, which in turn could be related to the steric environment of Ti. For example, one could hypothesize that the more thermodynamically stable trans isomer is formed in the presence of the unhindered Cp ligand, while the cis isomer is produced as a consequence of some steric constraint imposed by the bulkier Cp* ligand, although also the counterion could play a role (cf. $Cp^*TiMe_3-B(C_6F_5)_3$ vs Cp^*TiCl_3-MAO).[21] Interestingly, the use of a *deactivated* styrene monomer such as *p*-chlorostyrene also favors the formation of the thermodynamically more stable isomer. The formation of some linear $C_{14}H_{20}$ oligomers is easily accounted for on the basis of the above mechanism, just assuming that occasionally a further ethylene molecule inserts into the metallacycloheptane intermediate before reductive elimination.

In this framework, the observed beneficial effect of $AlMe_3$ for the production of the co-oligomers could be not limited to a trivial function as impurity scavenger, but could be related to some reaction with Ti: actually, the ability of $AlMe_3$ to coordinate to cationic complexes, affording μ-Me bridged bimetallic species, was reported by Bochmann[22] for cationic metallocenes and was recently observed even in the case of $Cp^*TiMe_3-B(C_6F_5)_3$.[17] This feature could favor the co-oligomerization, e.g., by depressing some competitive reaction (such as homopolymerization) or even by increasing the selectivity toward the reduction of Ti(IV) to the proposed Ti(II) active species.

The origin of the branched $C_{14}H_{20}$ oligomer is less easily explained: one should hypothesize the in-situ formation of some 1-butene (see Scheme 3), which (i) would coordinate to Ti(II) together with a styrene molecule; (ii) oxidative addition would produce a 4-ethyl-2-phenyl-titanacyclopentane, followed by (iii) further insertion of ethylene at the less hindered site affording a 4-ethyl-2-phenyltitanacycloheptane; finally, (iv) reductive elimination would yield 3-ethyl-1-phenyl-1-hexene. Of course, the proposed mechanism is tentative at this moment, although it seems better suited than more conventional insertion/elimination pathways to account for the experimental data. Also, the regiochemistry leading to 2-phenyl- and 3-alkylmetallacyclopentane has precedent in related zirconocene chemistry.[23] Strong support to our working hypothesis would come from the identification and synthesis of suitable Ti(II) complexes able to oligomerize olefins via metallacycle intermediates.

Conclusions

Analysis of the organic layers obtained after hydrolysis of E−S copolymerization runs performed with the $Cp^*TiMe_3-B(C_6F_5)_3$ catalytic system has revealed the presence of several unsaturated oligomers, which have been fully characterized by different techniques, such as NMR and GC-MS. The main components are two trimers containing two E and one S units, namely *cis*-1-phenyl-1-hexene and 6-phenyl-1-hexene, and one branched tetramer containing three E and one S units, namely 3-ethyl-1-phenyl-1-hexene. Thus, the previously reported[11] polyethylene with 4-phenyl-1-butyl branches, which is formed in the same reaction medium, derives from copolymerization of the in situ produced 6-phenyl-1-hexene with ethylene. Of course, the other co-oligomers, which are internal olefins, are not incorporated in the polymer. Similar results have been obtained with catalysts based on other half-titanocenes activated by methylalumoxane. Optimization of the reaction conditions for the $CpTiCl_3$−MAO catalyst results in styrene conversions to unsaturated oligomers >90%. Interestingly, in the presence of the latter catalyst only *trans*-1-phenyl-1-hexene is formed as the internal olefin, at variance with systems containing the bulkier Cp* ligand. Dual-catalyst systems, with one component producing the unsaturated oligomers and the latter copolymerizing the formed α-olefin with ethylene, have been successfully tested to produce selectively polyethylene with 4-phenyl-1-butyl branches. Several substituted styrenes, i.e., *p*-methylstyrene, *p*-*tert*-butylstyrene, *p*-chlorostyrene, and *m*-methylstyrene, have been tested in the copolymerization with ethylene under similar conditions, affording polyethylenes having the corresponding 4-aryl-butyl branches as well as oligomeric fractions analogous to those obtained from styrene. Finally, a mechanism involving Ti(II) active species and metallacycle intermediates has been proposed to account for the observed selectivity in the co-oligomerization as well as for the related selective trimerization of ethylene to 1-hexene.[19] Work is in progress in order to identify and synthesize Ti(II) complexes able to selectively co-oligomerize ethylene and styrene.

Experimental Section

General. Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk or glove-box techniques. Polymerization grade ethylene was used without further purification. Styrene and substituted styrenes were purified by distillation under reduced pressure over CaH_2. Toluene was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Methylalumoxane (Aldrich) was purchased as a 10 wt % solution in toluene and stored as a solid in a glovebox after the solvent was removed under reduced pressure. $CpTiCl_3$, Cp^*TiCl_3, $(Ind)TiCl_3$, Cp^*TiMe_3, and $B(C_6F_5)_3$ were prepared according to the literature.[24]

Copolymerizations. The copolymerization runs were carried out at atmospheric pressure in 100 mL glass flasks provided with a magnetic stirrer. The reactor was charged under nitrogen sequentially with toluene, styrene, $AlMe_3$ (as a scavenger), or MAO in the amounts specified in Tables 1 and 3; the inert gas was removed, and the polymerization mixture was saturated with ethylene (which was continuously fed during the run) and thermostated at the desired temperature. The reaction was initiated by injecting simultaneously into the flask Cp^*TiMe_3 and $B(C_6F_5)_3$ (runs 1−6) or $Cp'TiCl_3$ (runs 7−22), as toluene solutions. The runs were stopped by injecting methanol, the reaction mixtures were poured in methanol, and the polymers were recovered by filtration, washed with fresh methanol, and dried under reduced pressure at 90 °C. The solutions resulting from methanolysis were shaken with water and heptane, and the organic layers were separated, dried over Na_2SO_4, and preliminarily analyzed by GC. Then the solvents and unreacted styrene were distilled off in a rotavapor at 80 °C, leaving liquid residues. A similar procedure was used for the copolymerizations of ethylene with substituted styrenes (runs 31−34). Runs 23−26 were carried out similarly, but the preisolated oligomeric fractions were used as the comonomer and metallocenes or "low-valency" catalysts were used (see Table 4). Runs 27−30 were carried out in two steps, charging a 100 mL glass flask sequentially with toluene, styrene, MAO, ethylene at atmospheric pressure, and $CpTiCl_3$; after 40 min (oligomerization step), to the reaction mixture was added a second metal complex (as specified in Table 5) and more MAO. The temperature was raised to 80 °C, and the mixture was stirred for a further 15 min with a continuous feed of ethylene (polymerization step). Then the run was stopped, and the reaction mixture was worked up as usual, yielding in any case some solid polymer.

Polymer Fractionation and Characterization. The raw copolymerization products were extracted by stirring with THF at room temperature. The THF-soluble fractions contain mainly the E−S (or ethylene-substituted styrene) alternating copolymer and some arylbutyl-branched PE, while the THF-insoluble fractions contain most of the arylbutyl-branched PE and some s-PS. The raw polymers and the different fractions were analyzed by NMR on an AM 250 Bruker spectrometer operating in the Fourier transform mode. The spectra were recorded in $C_2D_2Cl_4$ at a temperature of 120 °C and referenced vs TMS using the resonance of the $S_{\delta+\delta+}$ carbons of the polymethylene sequences (δ = 30.0 ppm) as a secondary standard. The ^{13}C NMR spectra of the polyethylenes with 4-(aryl)-1-butyl branches are very similar to the spectrum displayed in Figure 8.

Analysis of the Oligomeric Fractions. GC analyses of the oligomeric fractions were performed on a DANI 3600 chromatograph equipped with a 30 m × 0.25 mm capillary column and a flame ionization detector. GC-MS was run on a FISONS GC 8000 instrument equipped with a 15 m capillary column DB-5ms.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C.

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