Enantioselectivity of C_s- and C_2-Symmetric *ansa*-Metallocene Catalysts in the Styrene Insertion

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ABSTRACT: The correlation between relative reactivity of the two styrene enantiofaces and geometry of *ansa*-zirconocene systems has been determined by ^{13}C NMR microstructural analysis of the poly(propylene-*co*-styrene−ethylene) (P/S−E) obtained in the presence of C_2- and C_s-symmetric zirconocene catalysts. The chemical shifts assignment accomplished by using configurational additivity rules suggests that secondary styrene insertion with C_2-symmetric metallocene occurs with the opposite enantioface with respect to primary propylene insertion. On the contrary the analysis of ^{13}C enriched copolymer obtained in the presence of C_s-symmetric catalyst seems to indicate that the secondary styrene insertion occurs with same enantioface with respect to propylene. This stereochemistry is what one expects for a simple olefin inserting in secondary fashion despite the peculiar behavior of the aromatic monomer toward zirconocene-based catalysts.

Introduction

The *ansa*-metallocene based catalysts generally promote the propylene polymerization through primary insertion of the monomer,[1] but depending on the catalytic precursor symmetry and on the aromatic ligands type, their enantioselectivity can be very different. As a matter of fact, a C_2-symmetric catalyst, containing the ethylenebis(1-indenyl) ligand bound to Mt, polymerizes propylene to isotactic polymer, whereas C_s-symmetric catalyst with Me_2C(cyclopentadienyl-9-fluorenyl) ligand produces syndiotactic polypropylene. The discrimination between the two enantiofaces of prochiral olefin (*re* and *si*)[1b,2] has been related in both cases to the chirality of the catalytic sites.[1,3]

Pino et al.,[4] by optical activity measurements on propylene hydrooligomers, proved that, in the case of the (*R, R*)[5] chirality of coordination of the tetrahydroindenyl ligand, the insertion of the *re* monomer enantioface is preferred. Molecular mechanics calculations carried out contemporary by Corradini and co-workers are in agreement with this result and suggest that the first C−C bond of the growing polymer chain plays a key role in determining the enantioselectivity.[6] Moreover, these authors reported predictions on the enantioselectivity of some catalytic systems containing several substituents in the different positions of indenyl ligand[7] and of the catalytic model with cyclopentadienyl-9-fluorenyl ligand.[8]

The picture becomes more complicated as one considers the stereochemistry when there are regioinverted insertions. It is well proved that occasional regioinversions of propylene insertion (secondary mode) occur with frequencies which depend on the catalytic system type.[9]

A complete determination of stereochemical configuration of the polymer chain containing the regioirregular units was obtained by NMR characterization of isotactic polypropylene prepared with C_2-symmetric metallocene catalysts. These studies showed that the isolated regioirregular units are prevailingly in *erythro* placement (Chart 1A)[9b,f] and that the *threo* placement arises from stereoinversion of the primary propylene following the secondary one (Chart 1B).[9f]

These analyses as well as molecular mechanics calculations[10] show that, for these isospecific catalysts, the secondary propylene insertion is highly stereospecific and occurs with opposite enantiofaces with respect to the primary insertion.

On the other hand, with respect to the regiospecificity of the C_s-symmetric *ansa*-metallocene catalysts, regioirregular monomeric units have not been detected by ^{13}C NMR in syndiotactic polypropylene obtained in the presence of these systems.[8,11]

Molecular mechanics calculations and more recent experimental results[12] with (*Z*)- and (*E*)-butene suggest that the intermediates energetically suitable for the secondary as well as for the primary insertions with these syndiospecific complexes coordinate monomer enantiofaces of the same chirality.[8b,c]

With respect to the styrene insertion, the ^{13}C NMR analysis of the end group shows that in the initiation step the regiospecificity of insertion of styrene into Zr−CH_3 is prevailingly secondary both in the case of ethylene-styrene copolymers prepared with the C_s-symmetric *ansa*-metallocene catalyst MePhC(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$[13] and, in the case of isotactic polystyrene samples obtained in the presence of the C_2-symmetric *ansa*-metallocene, *rac*-Me_2C-bis(1-indenyl)-$ZrCl_2$.[14] Moreover in P/S−E copolymerization promoted by the C_2-symmetric *ansa*-metallocene *rac*-ethylenebis(1-indenyl)$ZrCl_2$, it has been found[15] that, also during the growing chain propagation steps, the insertion of the styrene is secondary.

To our knowledge, no experimental data about the correlation between relative reactivity in polymerization of the two styrene enantiofaces and geometry of *ansa*-metallocene systems have been reported in the literature. Such a correlation deserves to be investigated by considering that at least the regiochemistry of insertion for this electron-rich monomer seems driven by electronic rather than by steric factors.

In the present paper, the enantioselectivity of C_s- and C_2-symmetric *ansa*-metallocene catalysts in the styrene insertion is determined by ^{13}C NMR characterization

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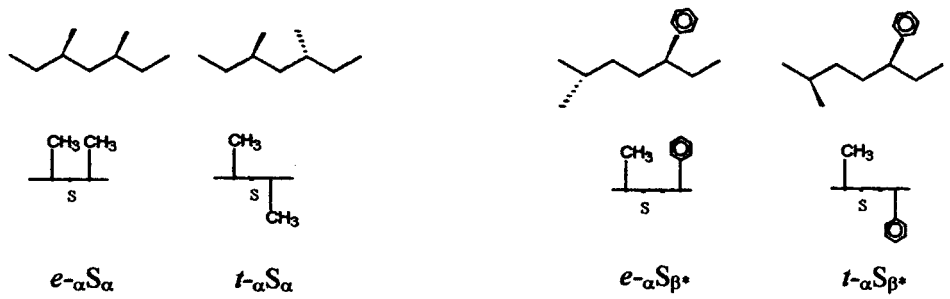


Figure 1. Trans-planar and Fisher projection representations of the chain segment costitued by two tertiary carbons (with methyl and/or phenyl substituents) in *erythro*- and *threo*-placement.

Chart 1

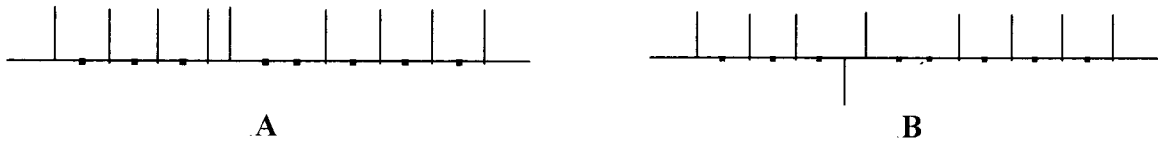


Chart 2

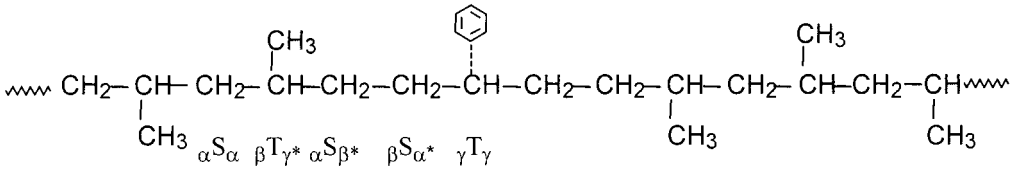
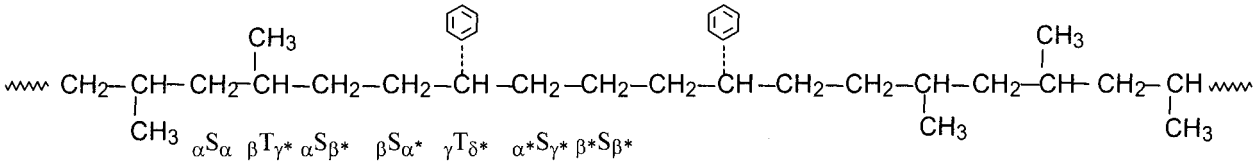


Chart 3



of P/S−E copolymers obtained in the presence of two systems: Me_2C(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$/MAO (**I**) and *rac*-ethylenebis(1-indenyl)$ZrCl_2$/MAO (**II**). The method we have adopted to gain this goal is the assignment of the relative configuration of the tertiary carbon atom bearing the phenyl ring (arising from styrene insertion) with respect to that of the tertiary carbon atom bearing the methyl group (arising from the insertion of the propylene).

Results and Discussion

Preliminary Remarks. To define the monomer enantiofaces, for the sake of clarity the *R, S* notation has been adopted in this paper according to refs 2b, 5a, and 16. With this notation, the enantiofaces of propylene and styrene with analogue steric requirements are indicated with the same symbol. On the contrary, due to the different rank of the methyl and phenyl groups for the priority rules, these faces are represented by opposite symbols in the *re, si* notation.

Each methylene carbon (S) of the copolymers has been labeled by two Greek letters, indicating the number of bonds separating it from the nearest tertiary carbons along the chain in both directions. To distinguish the two sides of the chain, the Greek letter has been positioned on the right or left side of the S letter. The Greek letter labeled by an asterisk indicates that the tertiary carbon bears a phenyl substituent (see Figure 1). The symbols *e* (*erythro*) or *t* (*threo*) have been used as configurational notation for tertiary carbons:[9b,17] if one considers a chain segment in trans-planar conformation, two tertiary carbons (with methyl and/or phenyl substituents) are in *erythro*-placement if the bonds with substituents are parallel each other (that is to say if they exhibit the substituents on the same side of the plane of the polymer chain in the Fisher projections).[18] Otherwise they are in *threo*-placement.

Enantioface Selectivity of the C_s-Symmetric System in the Styrene Insertion. The P/S−E copolymerization has been performed in the presence of the syndiospecific catalyst **I**. The aliphatic region of the ^{13}C NMR spectrum of a copolymer P/S−E is displayed in Figure 2. The pattern of signals is consistent with the copolymer structure of syndiotactic polypropylene sequences jointed by one or more styrene−ethylene sequences, hereafter called joints (Chart 2 and Chart 3). Consequently, also with this catalyst system the insertion of styrene during the growing chain propagation step is secondary.

The stereochemical structures of the joints depend on the enantioface selectivity of the two sites in the styrene insertion with respect to the propylene insertion. In particular the C_s-symmetric system **I** presents two enantiotopic sites at the transition metal favoring the coordination of a prochiral monomer with one of its two faces (the *R* chirality at metal should favor the *R* coordination of the propene; the *S* chirality at metal the *S* coordination).[8] In a chain migratory insertion mechanism,[3c,11a] the two enantiofaces (*R* and *S*) alternate regularly at each insertion.

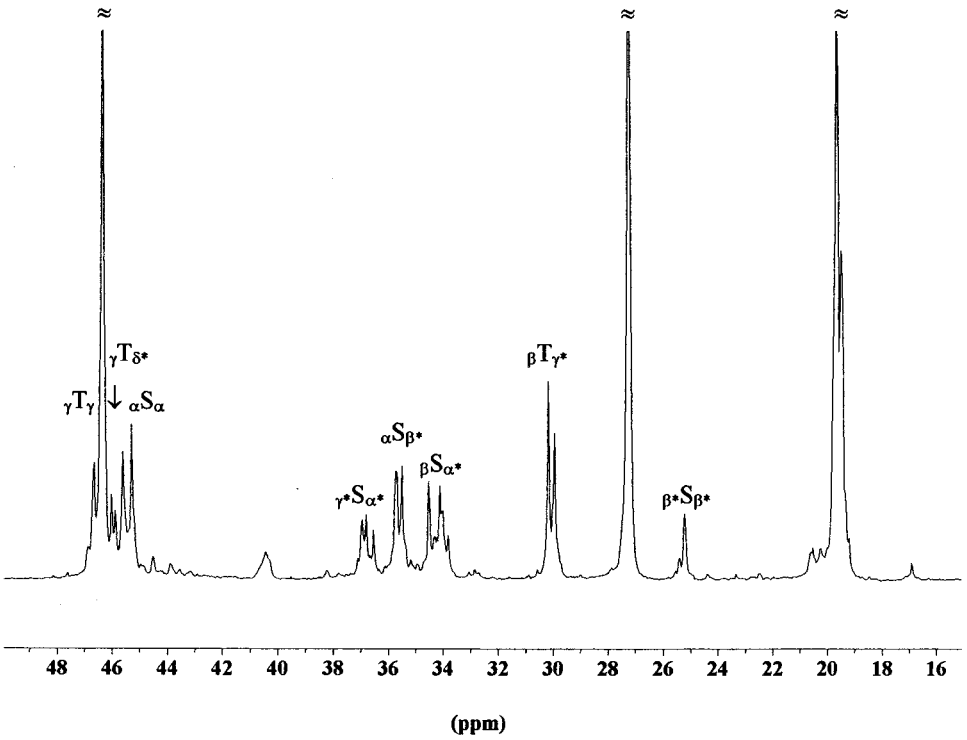


Figure 2. Aliphatic region of ^{13}C NMR spectrum of the copolymer prepared with **I** (see Charts 2 and 3). TMS scale.

Chart 4

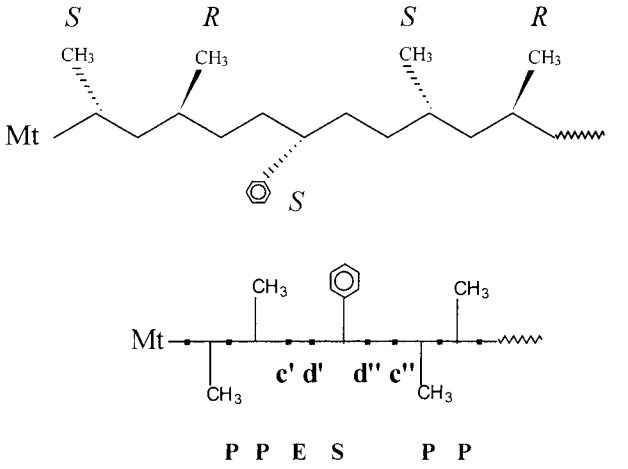


Chart 5

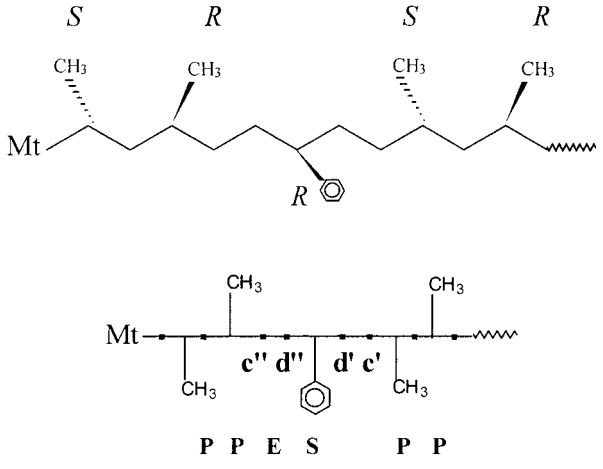
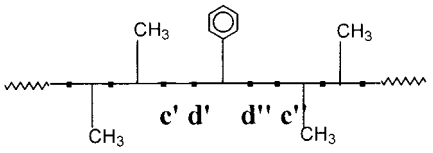


Chart 6



The sequence of the styrene insertion and the subsequent ethylene insertion (see Chart 2) bridges the insertions of two opposite propylene enantiofaces. The *R*-styrene insertion and the *S*-styrene insertion into the site that favors the *R*-propylene insertion are displayed in Chart 4 and in Chart 5, respectively.

If one does not consider the direction of the chain growth the stereostructures of the joints arising from insertion of two different styrene enantiofaces are equivalent (Chart 6).

As a consequence of the different stereochemical environments, one can observe the resonances of the $_{\alpha}S_{\beta^*}$ and the $_{\alpha^*}S_{\beta}$ in the ^{13}C NMR spectrum (Figure 2) split into two doublets, at $\delta = 35.7_6$, 35.5_6 ppm (**c′** and **c″**) and 34.5_6, 34.16 ppm (**d′** and **d″**) respectively (see the ^{13}C NMR assignment section). This splitting is the key for the determination of the stereochemistry of the styrene insertion when one has identified the direction of chain grown.

To identify the direction of the growth of the polymer chain and consequently to discriminate between the two situations sketched in the Charts 4 and 5, we need to distinguish between the $_{\beta^*}S_{\alpha}$ and $_{\beta}S_{\alpha^*}$ arising from ethylene units and those arising from propylene and styrene units. For this purpose, a P/S−E copolymer has been prepared in the presence of the system **I** under conditions similar to those of sample 1, but using ethylene 42% enriched with ^{13}C (sample 2). In Figure 3 are shown the spectra of sample 1 (A) and sample 2 (B), in the region where the $_{\alpha}S_{\beta^*}$ and $_{\alpha^*}S_{\beta}$ resonate. From the high intensities of the signals at $\delta = 34.1_6$ and 35.5_6 ppm in the spectrum of the sample 2 one can safely affirm that **d″** and **c″** belong to the ethylene units.

This result is in agreement with the stereochemical sequence described in Chart 4, where the styrene and

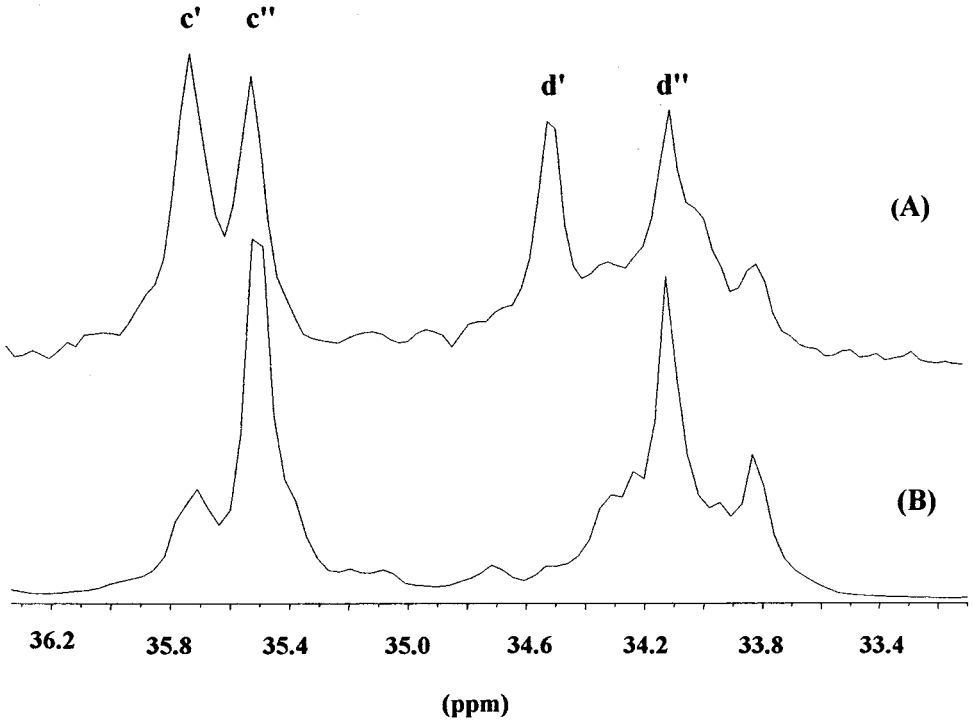


Figure 3. ^{13}C NMR spectra of the copolymer prepared with **I** (see Experimental Section) expanded in the region where the $_{\alpha^*}S_{\beta}$ and $_{\alpha}S_{\beta^*}$ resonate: (A) sample 1 (14-fold vertically expanded); (B) sample 2, obtained with ethylene-1-^{13}C. TMS scale.

Chart 8

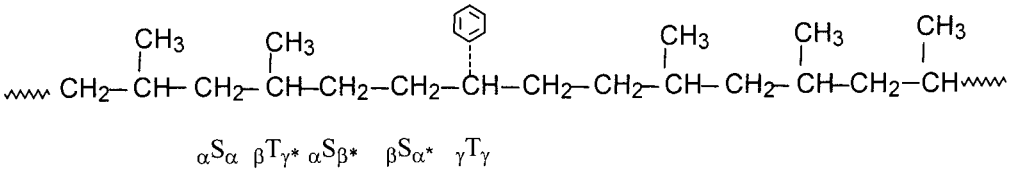
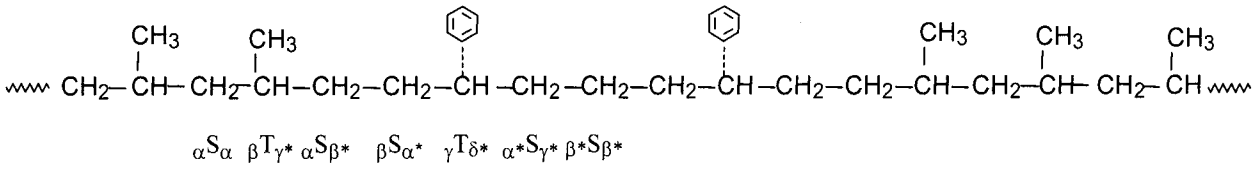
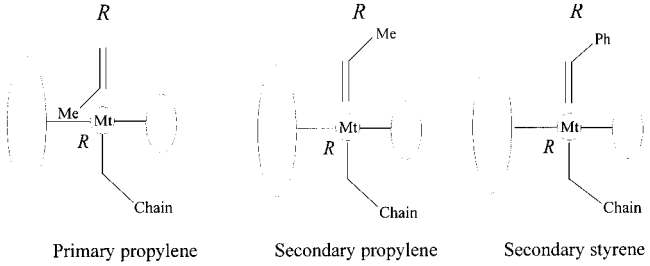


Chart 9



propylene insertions into the same site are such as to generate a *threo* placement of the styrene and propylene units spanning the ethylene unit. The above observation leads to the following conclusion: *the secondary styrene insertion occurs with the same enantioface with respect to the primary propylene insertion on C_s-symmetric metallocene*. It is worth noting that such behavior is analogous to that foreseen for the secondary propylene insertion (see Chart 7).[8b,c]

Chart 7



Enantioface Selectivity of the C_2-Symmetric System in the Styrene Insertion. As previously reported[15] the P/S−E copolymers prepared with **II** feature isotactic polypropylene sequences jointed by one or more styrene−ethylene sequences (see Charts 8 and 9).

In Charts 10 and 11 are shown the two possible stereostructures of the joint of the copolymer obtained in the presence of the catalyst system **II** arising from styrene and propylene insertion with the same and opposite enantiofaces, respectively.

The spectrum of the copolymer (Figure 4) shows only two sharp resonances for $_{\alpha^*}S_{\beta}$ (33.9_2 ppm) and $_{\alpha}S_{\beta^*}$ (34.5_6 ppm). This fact indicates that only one of the two possible stereostructures is present. To identify the stereostructure more consistent with the experimental NMR data, the chemical shifts of the methylene carbons **d** and **c** of Charts 10 and 11 have been calculated as reported in ^{13}C NMR assignment section. The comparison between the calculated and the experimental chemical shifts is shown in Table 1. One can observe that the experimental values of the $34,5_6$ ppm (methylene **c**) and $33,9_2$ ppm (methylene **d**) are in agreement with the chemical shifts calculated for the stereostructure of Chart 10.

Chart 10

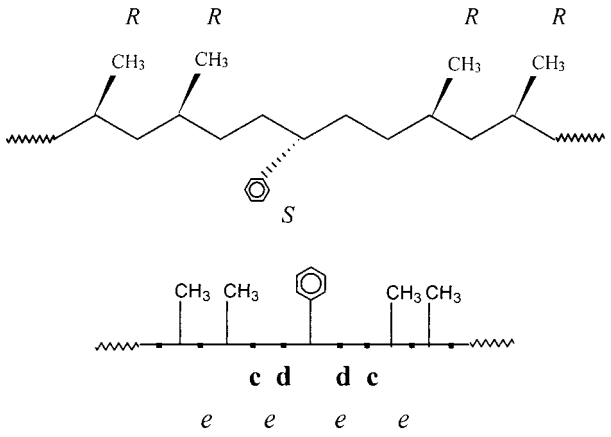


Chart 11

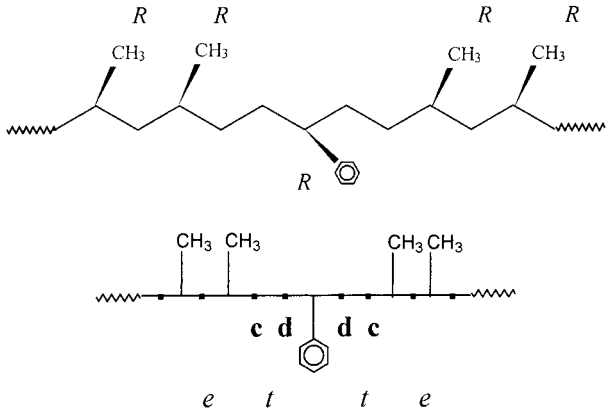
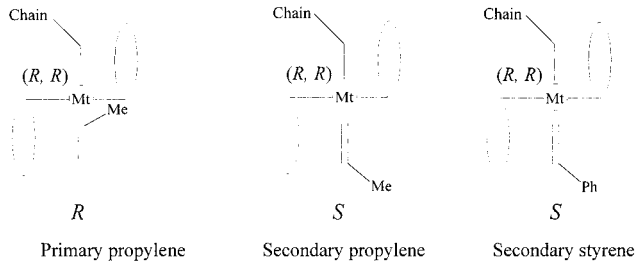


Chart 12



Consequently, on the basis of the stereostructure of Chart 10 it's possible to conclude that *the secondary styrene insertion occurs with the opposite enantioface with respect to the primary propylene insertion on C_2-symmetric metallocene*. Therefore, with the C_2-symmetric metallocene the preferred styrene enantioface is the same observed[9b,f] and calculated[10] for secondary propylene insertion (see Chart 12).

^{13}C NMR Assignments. Zambelli and Gatti[17] proposed the following relationship for the prevision of the chemical shifts of the methyl group belonging to an hydrocarbon chain

$$\nu = \nu_0 + \sum N_i P_i + \sum R_{ij}$$

where ν_0 is the chemical shift of the methyl group bound to the tertiary carbon inside a polymethylene chain, N_i *is the number of methyl groups having a definite distance from and a steric relation with the observed methyl, P is the additivity parameter characterizing both the distance and the steric relationship, and R_{ij} is a parameter which describes the effect of the proximity of the two methyl substituents and it is dependent on the their steric relationship.*

Afterward Cheng and Bennett[19] proposed a similar relationship for the methylene carbons:

$$\nu = \nu_0 + \sum A_i + \sum R_{ij} \quad (1)$$

In this relationship, the chemical shift of the methylene carbon of the polymethylene chain (ν_0) is added by a contribution due to the presence of methyl substituents ($\sum A_i$) and to the relative configuration of the tertiary carbons bearing the substituents ($\sum R_{ij}$). As a consequence the difference between the chemical shifts of the carbon atoms constitutionally equivalent arises from the difference of the configurational contributions:

$$\nu_{cx} - \nu_{cy} = (\sum R_{ij})_{cx} - (\sum R_{ij})_{cy} \quad (2)$$

The values of the parameters R_{ij} of polyolefins are reported in the literature[19] and can be acquired from the ^{13}C NMR spectra of the model compounds reported by Zambelli et al.[20]

In this paper the above relationships are extended to methylene carbons of hydrocarbon chains having phenyl substituents in addition to the methyl substituents.

So for **c″, c′, d′,** and **d″** of Chart 6 the following relationships can be written:

$$\nu_{\mathbf{c}''} = C + t\text{-}R_{\alpha\gamma} + t\text{-}_{\alpha}R_{\beta^*} + e\text{-}R_{\beta^*\epsilon}$$

$$\nu_{\mathbf{c}'} = C + t\text{-}R_{\gamma\alpha} + e\text{-}_{\beta^*}R_{\alpha} + t\text{-}R_{\beta^*\epsilon}$$

$$\nu_{\mathbf{d}''} = D + t\text{-}R_{\delta\beta} + t\text{-}_{\alpha^*}R_{\beta} + e\text{-}R_{\alpha^*\delta}$$

$$\nu_{\mathbf{d}'} = D + t\text{-}R_{\delta\beta} + e\text{-}_{\beta}R_{\alpha^*} + t\text{-}R_{\alpha^*\delta}$$

where $C = \nu_0 + \sum A_i$; $D = \nu_0 + \sum A_i$.

The difference between the **c**-type carbons and between the **d**-type carbons is given by the difference of the R_{ij^*} parameters:

$$\nu_{\mathbf{c}'} - \nu_{\mathbf{c}''} = (t\text{-}R_{\epsilon\beta^*} - e\text{-}R_{\epsilon\beta^*}) - (t\text{-}_{\alpha}R_{\beta^*} - e\text{-}_{\alpha}R_{\beta^*}) = F_{\beta^*\epsilon} - {}_{\alpha}F_{\beta^*} \quad (3)$$

$$\nu_{\mathbf{d}'} - \nu_{\mathbf{d}''} = (t\text{-}R_{\alpha^*\delta} - e\text{-}R_{\alpha^*\delta}) - (t\text{-}_{\alpha^*}R_{\beta} - e\text{-}_{\beta}R_{\alpha^*}) = F_{\alpha^*\delta} - {}_{\alpha^*}F_{\beta} \quad (4)$$

where

$$F_{ij^*} = t\text{-}R_{ij^*} - e\text{-}R_{ij^*} \quad (5)$$

To acquire the values of F_{ij^*} the chemical shifts of the 3-methyl-6-phenyloctane diasteroisomers have been compared as shown in Table 2.

In Table 3 the F_{ij} values calculated from the ^{13}C NMR of 3-methyl-6-phenyloctane diasteroisomers and from literature data are reported that are useful for the subsequent analysis of the P/S−E copolymers.

Copolymers Obtained with System I. The signals at $\delta = 34.5_6$ ppm and $\delta = 34.16$ ppm in the ^{13}C NMR spectrum of sample 1 (Figure 2) have been assigned to **d′** and **d″** respectively by substituing in eq 4 the values reported in Table 3. The calculated difference ($\nu_{\mathbf{d}'} - \nu_{\mathbf{d}''} = 0.4$ ppm) is in agreement with the observed one. From analogy we assigned the signals at $\delta = 35.7_6$ ppm to **c′** and $\delta = 35.5_6$ ppm to **c″**. Such an assignment has been confirmed by the resonances of the ^{13}C enriched copoly-

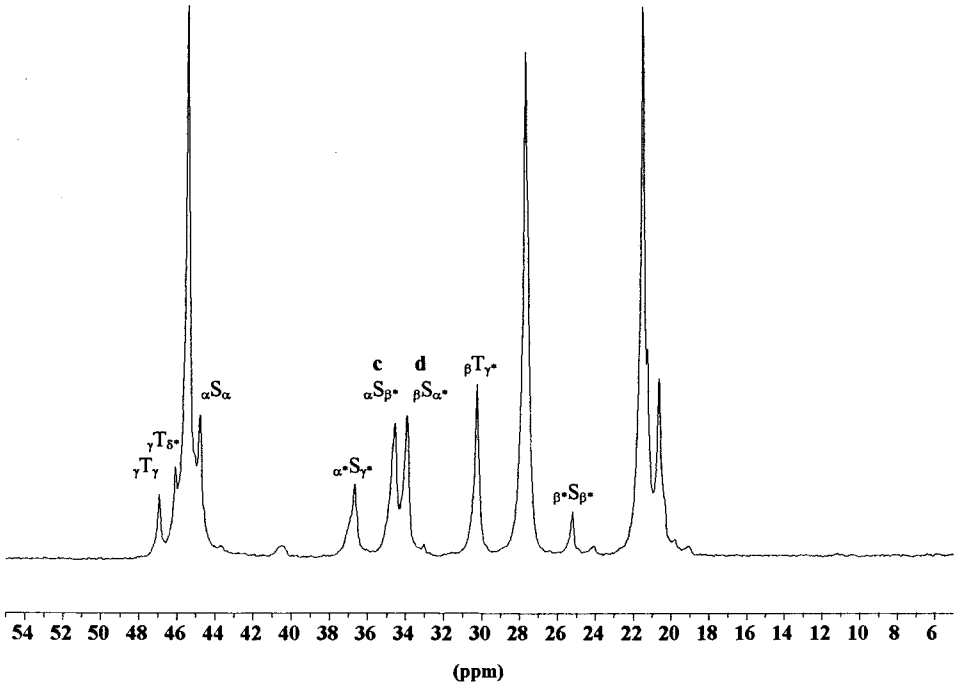


Figure 4. Aliphatic region of ^{13}C NMR spectrum of the copolymer prepared with **II** (see Charts 8 and 9). TMS scale.

Table 1. ^{13}C NMR Chemical Shifts of the Joints of the Copolymer Obtained with System II (TMS Scale)

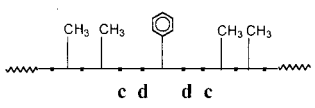
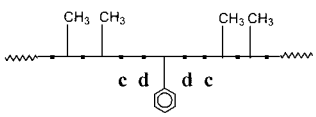
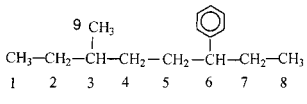
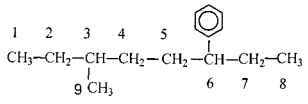
 calculated (ppm)		 calculated (ppm)		experimental chemical shifts (ppm)	
c[10]	**d**[10]	**c**[11]	**d**[11]	**c**	**d**
34.6	33.9	35.2	34.5	34.5_6	33.9_2

Table 2. Chemical Shifts (δ in ppm) of the Aliphatic Carbons in 3-Methyl-6-phenyloctane



S (*R*) *R* (S)



R (*S*) *R* (*S*)

carbon type[a]	(*R*, *S*) + (*S*, *R*)[b]	(*R*, *R*) + (*S*, *S*)[b]
1	11.41	11.41
2	29.50	29.65
3	34.47	34.47
4	34.39	34.57
5	33.84	33.95
6	48.14	48.23
7	28.66	29.13
8	12.19	12.19
9	19.24	19.10

[a] For the assignment see the Experimental Section. [b] The mixture of the (*R*, *S*) + (*S*, *R*) and (*R*, *R*) + (*S*, *S*) isomers simulate the *erithro* and the *threo* joints of the P/S−E copolymer, respectively.

mer (sample 2, Figure 3) where the enhanced peaks are at 35.5_6 and 34.1_6 ppm (**c**″ and **d**″).

Table 3. F_{ij} Parameters Calculated from Table 2 and from the Literature Data

methylene carbons	F_{ij} (ppm)	
$S_{\alpha^*\delta}$	$F_{\alpha^*\delta}$	0.5
$S_{\alpha\delta^*}$	$F_{\alpha\delta^*}$	0.1_5
$_{\alpha^*}S_{\beta}$	$_{\alpha^*}F_{\beta}$	0.1
$_{\alpha}S_{\beta^*}$	$_{\alpha}F_{\beta^*}$	0.2
$S_{\beta\delta}$	$F_{\beta\delta}$	0.2^{20}
$S_{\alpha\gamma}$	$F_{\alpha\gamma}$	0.8^{20}

Copolymers Obtained with System II. The above relationships have been used to calculate the chemical shifts of the $_{\alpha}S_{\beta^*}$ and the $_{\alpha^*}S_{\beta}$ in the stereochemical environments shown in Charts 10 and 11. The result has been obtained by starting from the chemical shifts of the structures of Chart 6.

The chemical shift difference between $\mathbf{d}^{11}$ (**d**, Chart 11) and **d**′ (**d**′, Chart 6) expected on the basis of eqs 2 and 5 should mainly depend on the difference between $F_{\beta\delta}$ and $_{\alpha^*}F_{\beta}$ as shown

$$\nu_{\mathbf{d}'} - \nu_{\mathbf{d}}{}^{11} = (t\text{-}R_{\beta\delta} - e\text{-}R_{\beta\delta}) - (t\text{-}_{\alpha^*}R_{\beta} - e\text{-}_{\alpha^*}R_{\beta}) = F_{\beta\delta} - {}_{\alpha^*}F_{\beta}$$

Table 4. Experimental Chemical Shifts of the Secondary Carbons of the Joints

	chemical shifts (ppm, ref TMS)	
carbon	system **I**	system **II**
c		34.5_6
c′	35.7_6	
c″	35.5_6	
d		33.9_2
d′	34.5_6	
d″	34.1_6	

and the chemical shift difference between $\mathbf{d}^{11}$ (**d**, Chart 11) and **d″** (**d″**, Chart 6) should depend on the difference between $F_{\beta\delta}$ and $F_{\alpha^*\delta}$:

$$\nu_{\mathbf{d}''} - \nu_{\mathbf{d}}{}^{11} = (t\text{-}R_{\beta\delta} - e\text{-}R_{\beta\delta}) - (t\text{-}R_{\alpha^*\delta} - e\text{-}R_{\alpha^*\delta}) = F_{\beta\delta} - F_{\alpha^*\delta}$$

In the same manner by comparison of the **c**-type carbon of Chart 10 and Chart 6, the result is

$$\nu_{\mathbf{d}'} - \nu_{\mathbf{d}}{}^{10} = (t\text{-}R_{\beta\delta} - e\text{-}R_{\beta\delta}) + (t\text{-}R_{\alpha^*\delta} - e\text{-}R_{\alpha^*\delta}) = F_{\beta\delta} + \mathrm{F}_{\delta\alpha^*}$$

$$\nu_{\mathbf{d}''} - \nu_{\mathbf{d}}{}^{10} = (t\text{-}R_{\beta\delta} - e\text{-}R_{\beta\delta}) + (t\text{-}{}_{\alpha^*}R_{\beta} - e\text{-}{}_{\alpha^*}R_{\beta}) = F_{\beta\delta} + {}_{\alpha^*}F_{\beta}$$

By substituting the experimental values of $\nu_{\mathbf{d}'}$,$\nu_{\mathbf{d}''}$ (see Table 4) and the values of the F_{ij} reported in Table 3, a chemical shift around 34.5 ppm is obtained for $\mathbf{d}^{11}$ while a chemical shift around 33.9 ppm is calculated for $\mathbf{d}^{10}$. The comparison with the experimental value (33.9_2 ppm, Table 1) seems to indicate that the configuration of the carbon **d** is that reported in Chart 10.

This result is confirmed by the analogous chemical shift previsions for the **c**-type carbon:

$$\nu_{\mathbf{c}'} - \nu_{\mathbf{c}}{}^{11} = (t\text{-}R_{\alpha\gamma} - e\text{-}R_{\alpha\gamma}) - (t\text{-}{}_{\alpha}R_{\beta^*} - e\text{-}{}_{\alpha}R_{\beta^*}) = F_{\alpha\gamma} - {}_{\alpha}F_{\beta^*}$$

$$\nu_{\mathbf{c}''} - \nu_{\mathbf{c}}{}^{10} = (t\text{-}R_{\alpha\gamma} - e\text{-}R_{\alpha\gamma}) + (t\text{-}{}_{\alpha}R_{\beta^*} - e\text{-}{}_{\alpha}R_{\beta^*}) = F_{\alpha\gamma} + {}_{\alpha}F_{\beta^*}$$

One can then calculate a chemical shift around 35,2 ppm for $\mathbf{c}^{11}$ and around 34.6 ppm for $\mathbf{c}^{10}$.

The experimental value of the 34.5_6 ppm (**c**, Table 1) is in agreement with the structure of Chart 10.

Conclusions

The ethylene as catalyst reactivator for the styrene incorporation into a polypropylene chain works well also with C_s-symmetric catalyst. A microstructure like that previously described for C_2-symmetric catalyst has been obtained but with syndiotactic polypropylene sequences. The use of ^{13}C-enriched ethylene allows one to observe stereospecific styrene insertion.

On the basis of stereochemical assignments of the ^{13}C NMR resonances, the enantioselectivity of the secondary styrene insertion with C_2- as well as with C_s-symmetric zirconocene catalyst seems to follow the observed or foreseen behavior of olefins such as propylene. As consequence of the results of Pino et al.[4] and of the calculations of Guerra et al.,[6−8,10] we can conclude that the (*R*, *R*) C_2-symmetric catalyst prefers *S*-styrene insertion, while with the C_s-symmetric catalyst, the *R* styrene enantioface is preferred at the *R* catalytic site.

Such a result is not obvious by considering the difference between propylene and styrene coordination at the metal. However a strictly olefinlike stereocontrol was previously observed for the alternating ethylene−styrene copolymerization with C_2- and C_s-symmetric catalysts but no information was achieved about the preferred monomer enantioface.

Regiochemical and stereochemical results similar to our findings with C_2-symmetric catalyst were reported by Rodewald and Jordan for styrene monoinsertion with the *rac*-ethylenebis(indenyl)Zr(η^2-6-Me-pyrid-2yl)(2-picoline) cation.[21]

Experimental Section

Materials. Ethylene-1-^{13}C (Isotec Inc., 99+% isotopic purity), ethylene, and propylene (Società Ossigeno Napoli, polymerization grade) were used without further purification. Toluene was refluxed for 48 h over metallic sodium and distilled under a nitrogen atmosphere. Styrene was purified by distillation under reduced pressure over CaH_2. Methylalumoxane was prepared by reaction of $Al(CH_3)_3$ with $FeSO_4 \cdot 7H_2O$ in toluene.[22] Me_2C(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$ and *rac*-ethylene-bis(1-indenyl)$ZrCl_2$ were prepared according to published procedure.[3c,23]

Copolymerizations. The synthesis of the copolymer prepared with *rac*-ethylene-bis(1-indenyl)$ZrCl_2$ catalyst is reported in ref 15. The two copolymers prepared with Me_2C(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$ catalyst were obtained by bubbling (0.10 L/min) the monomers mixture (ethylene−propylene 1/20), prepared with an automatic gas blending device (MKS Instruments, Deutschland GmbH), at atmospheric pressure into a 100 mL Pyrex reactor provided with magnetic stirrer, containing toluene (10 mL), styrene (20 mL), MAO (7×10^{-3} mol), and catalyst (7×10^{-6} mol) at 0 °C for 4 h. The copolymers were coagulated by pouring the reaction mixture into methanol acidified with HCl (aqueous, concentrated) and then filtered, washed with fresh methanol, and vacuum-dried. The gas mixtures of the monomers were analyzed by gas chromatography. Ethylene 42% enriched with ^{13}C, used for sample 2, was obtained by diluting the ethylene 99% ^{13}C enriched with ethylene in natural isotopic composition. Yield: 0.2 g for both samples.

Synthesis of 3-Methyl-6-phenyloctane. The commercial *racemic* 2-phenylbutanoic acid (Aldrich) was dissolved in methanol in the presence of sulfuric acid and kept under reflux overnight to give the methyl ester. The reduction of the ester to 2-phenylbutan-1-ol was performed by using $LiAlH_4$ in tetrahydrofuran. The resulting alcohol was added to a suspension of pyridiniumdichromate in dichloromethane. The mixture was well stirred at room temperature for 120 min, diluted with diethyl ether, and filtered through a glass filter filled with silica gel containing $CaSO_4$ (10%) (silicagel G, Merck, Darmstadt, Germany). Removal of the solvent gave the pure 2-phenylbutanal.[24,25] The commercial *racemic* 2-methybutan-1-ol (Aldrich) was treated with $SOCl_2$ and pyridine and kept overnight with stirring at 90 °C. From the reaction mixture the 1-chloro-2-methylbutane was separated and purified by distillation under reduced pressure. The Grignard reagent of this compound, prepared in tetrahydrofuran, was kept 12 h to react with the 2-phenylbutanal. The product of this reaction, 3-phenyl-6-methyloctan-4-ol, was converted into 3-methyl-6-phenyl-octane through esterification with *p*-toluenesulfonyl chloride and subsequent hydrogenolysis with $LiAlH_4$.[26] The reaction products were isolated by chromatography on silica (by eluting with petroleum ether 40−60 °C) and identified by mass and ^{13}C NMR spectroscopy as a 3:2 mixture of the diastereoisomers (*R*, *S*) + (*S*, *R*) and (*R*, *R*) + (*S*, *S*), respectively. The pattern of signals relative to the more abundant isomers was assigned to the (*R*, *S*) + (*S*, *R*) mixture on the basis of the general behavior of the chemical shifts in hydrocarbon diastereoisomers.[19,20,25,27]

^{13}C NMR Analysis. The ^{13}C NMR spectra of all samples were recorded under strictly identical conditions on an AV 400

Bruker operating at 100 MHz in the Fourier transform mode and at 293 K. The samples (30 mg) were dissolved in 0.5 mL of $CDCl_3$ into a tube with 5 mm outer diameter. Tetramethylsilane (TMS) was used as an internal chemical shift reference.

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