Ethene/4-Methyl-1-pentene Copolymers by Metallocene-Based Catalysts: An Insight in ^{13}C NMR Assignment

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ABSTRACT: This paper presents a ^{13}C NMR investigation of a series of ethylene/4-methyl-1-pentene copolymers, prepared with the metallocene precatalyst, *rac*-$CH_2(3\text{-}^tBuInd)_2ZrCl_2$ and having a 4-methyl-1-pentene content spanning from 1 to 35% by moles. The high stereoregularity and the complete regioregularity obtained with this catalyst greatly simplify the spectra, as the spectral multiplicity can be ascribed to differences in comonomer sequences only. Previously assigned chemical shifts have been checked and novel sequence assignments have been obtained. The sequence assignment is based on: (i) comparison of the copolymer chemical shifts with those of the spectrum of the 4-methyl-1-pentene homopolymer obtained with the same catalyst, (ii) DEPT experiment on one significant sample, (iii) comparison of spectral intensities of samples of different compositions, (iv) correlation between integrated peak areas of signals of sequences linked by stoichiometric relationships, (v) comparison with selected signals of the spectrum of a sample of ethylene/4-methyl-1-pentene copolymer obtained with a different catalyst. Correct assignment of $S_{\beta\beta}$, $S_{\alpha\gamma}$, and $S_{\alpha\delta}$ methylene carbons allows for a precise measurement of the entire set of methylene peak areas present in the copolymers studied in this paper, and consequently, a correct determination of dyad and triad copolymer composition and of comonomer content.

Introduction

Ethylene/4-methyl-1-pentene copolymers are considered an attractive polyolefin material as having better mechanical properties and processability than the commercial ethylene/linear α-olefin copolymers.[1] The interest in these copolymers especially arises from the bulky branched substituent that is expected to lower the melting point and density of polyethylene more effectively than linear α-olefins (e.g., 1-butene, 1-hexene, and 1-octene) at similar level of incorporation.[2] In the past thirty years, attempts have been made to produce well-defined ethylene/4-methyl-1-pentene (4M1P) copolymers by using traditional heterogeneous Ziegler−Natta catalysts. However, the copolymers so produced show rather low comonomer incorporation and in addition are heterogeneous with regard to comonomer incorporation, copolymer composition, and molecular weight distribution.[3,4]

The introduction of the metallocene catalysts has disclosed a new chapter in the history of polyolefins. Metallocene catalysts make it possible to obtain stereoregular polymers with a predetermined structure. Moreover, ethylene/α-olefin copolymers are uniform in composition and have controlled comonomer incorporation even when comonomers are as bulky as 4M1P.

The more recently discovered constrained geometry catalysts of monocyclopentadienylamido (CpA)−titanium complexes has broken out a further improvement in copolymerization performance of 4-methyl-1-pentene comonomer.[5−8] In fact CpA catalysts give a higher level of 4-methyl-1-pentene incorporation in conjunction with higher activity and molecular weight with respect to conventional metallocenes.[9] The easy incorporation of higher α-olefins by these catalysts appears to be a consequence of the sterically accessible nature of the coordination site.[10] The precatalyst $Me_2Si(\eta_5\text{-}C_5Me_4)\text{-}(\eta_1\text{-}N\text{-}^tBu)TiCl_2$ is considered to be the commercial standard for ethylene/higher α-olefin copolymerization. At present, it is increasingly used for producing commercial polyolefin plastomers.

Very recently, sterically expanded zirconium fluorenyl−amido complexes have been developed that have been shown to incorporate 4-methyl-1-pentene at unprecedented levels: ethylene results nearly twice more reactive than 4-methyl-1-pentene.[11−12]

All of these novelties lead to renewed interest in ethylene/4-methyl-1-pentene copolymers, as they open the way to commercializing of such interesting materials. This also hinges on the availability of a good analytical methodology for measuring ethylene/4-methyl-1-pentene sequence distribution in these copolymers.

Starting from the fundamental work by Carman and Wilkes[13] and by Randall,[14] extremely detailed assignments of ^{13}C NMR signals of ethylene/linear α-olefin copolymers have been conducted over the years, up to recent papers in which sophisticated NMR techniques are used for unequivocal assignment of comonomer sequences.[15] On the contrary, to the best of our knowledge, the ^{13}C NMR assignment of the spectra of ethylene/4-methyl-1-pentene copolymers still relies on a pioneering work by Kimura et al. of 1984.[3,16] In those years, only ethylene/4-methyl-1-pentene copolymers produced with conventional Ziegler−Natta catalysts were available. Kimura et al. based their sequence assignment of the ^{13}C NMR spectra on three copolymers containing 2.0, 11.8, and 19.4% by moles of 4-methyl-1-pentene obtained as ethyl acetate, ethyl ether, and heptane extracts, respectively, from a commercial product (Mitsui Petrochemical Co.). Because of the heterogeneity of Ziegler−Natta catalysts, these copolymer fractions are actually produced by different kinds of active sites and are likely different not only in comonomer content but in chain stereoregularity and comonomer distribution as well, thus they are not fully suitable for the purpose of sequence assignment. Homogeneous metallocene catalysts have opened the possibility of synthesizing series of ethylene/4-methyl-1-pentene copolymers with identical chain stereoregularity and comonomer distribution and only differing in comonomer content, so facilitating the comonomer sequence assignment.

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Scheme 1

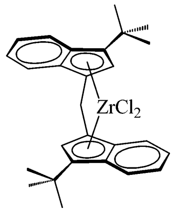


Table 1. Ethylene/4-Methyl-1-pentene Copolymers Obtained with *rac*-CH$_2$(*t*-BuInd)ZrCl$_2$/MAO as Catalytic System[a]

run	$[P]_{feed}$ (M)	activity × 10^{-3} ($mg_{pol}/mmol_{Zr} \times h$)	t_{pol} (min)	$[P]_{copolymer}$[b] (mol %)
1	0.15	316.0	30	1.2
2	0.30	120.0	30	2.1
3	0.59	136.3	15	4.9
4	1.19	67.7	30	9.3
5	1.98	7.2	60	13.5
6	3.56	38.4	30	34.9

[a] Polymerization conditions: solvent = toluene, total volume = 100 mL, Al/Zr = 1000 (mol/mol), $T = 45$ °C, $P = 2.47$ atm, [catalyst] = 10 μmol. [b] 4-Methyl-1-pentene content calculated from ^{13}C NMR spectra.

Here we present a ^{13}C NMR investigation of a series of ethylene/4-methyl-1-pentene copolymers prepared with the metallocene catalyst, *rac*-CH$_2$(3-^{t}BuInd)$_2$ZrCl$_2$.[17−18] The copolymer microstructure obtained with this catalyst, first developed by Resconi for the synthesis of completely regio- (% 2,1 = 0) and highly stereo(iso)-specific (% *mmmm* = 97) polypropene,[17] greatly simplifies the spectra as the spectral multiplicity can be ascribed to differences in comonomer sequences only. This study gives us the chance for checking the previously assigned chemical shifts and for making new sequence assignments.

The sequence assignment is based on: (i) comparison of the copolymer chemical shifts with those of the spectrum of the 4-methyl-1-pentene homopolymer obtained with the same catalyst, (ii) DEPT experiment on a significant sample, (iii) comparison of spectral intensities of samples of different compositions, (iv) correlation between integrated peak areas of signals of sequences linked by stoichiometric relationships, and (v) comparison with selected signals of the spectrum of a sample of ethylene/4-methyl-1-pentene copolymer obtained with a different metallocene catalyst.

On the basis of the set of assignments of comonomer sequences being as detailed as possible, obtained by our procedure, it should be easier to ascribe the presence of further signals appearing in the spectra of copolymers obtained with commercial regio- and stereospecific catalysts to steric effects or to comonomer inversions. This will be the object of our future work.

Results and Discussion

A series of ethylene/4-methyl-1-pentene (from now on **E/P**) copolymers with different comonomer composition was prepared with the sterically hindered, highly stereospecific and completely regiospecific [*rac*-CH$_2$(3-^{t}BuInd)$_2$ZrCl$_2$]/methylaluminoxane (MAO) catalyst.

In Table 1, data of **E/P** copolymerizations performed are reported along with the polymerization conditions. The relative ratio of ethylene and 4-methyl-1-pentene in the polymerization bath covered a wide range, allowing for the preparation of copolymers with a 4-methyl-1-pentene content from about 1% to about 35% by moles.

In Figure 1, the spectra of poly-4-methyl-1-pentene (a) and of copolymers containing 2.1% (b), 9.3% (c), and 34.9% (d) comonomer moles, respectively, are shown. The carbon terminology follows that of Carman and Wilkes,[13] where S, T, and P refer respectively to the secondary (methylene), tertiary (methine), and primary (methyl) carbons of the main chain. The two Greek subscripts indicate the distances of the carbon in question from the neighboring methines, where δ indicates all methines farther than three bonds from the methylene carbon of interest. Methylene and methine carbons in the side chain are designated by the symbols CH$_2$(sc) and CH(sc) (Scheme 2). A DEPT experiment performed on a copolymer having 13.5 mol % 4-methyl-1-pentene content is shown in Figure 2, where the carbon signals of even multiplicity (methylene carbons) appear 180° opposite in phase with respect to carbon signals of odd multiplicity (methyl and methine carbons) and are thus unequivocally distinguished.

All of the chemical shifts assignments are listed in Table 2. The chemical shifts and the chemical shift differences are compared with those given in the literature.

In the following, the previous assignments of the secondary and tertiary carbons of the main chain are first checked and the differences from literature discussed. Then the spectral regions that regard methyl, methylene CH$_2$(sc), and methine CH(sc) carbons of the side chain are analyzed in detail. These spectral regions, that regard **P** centered sequences, are better resolved. The assignment and, in some cases, the quantitative evaluation of sequences as long as tetrads and pentads are possible.

Main Chain Region. The analysis of the spectra of copolymers with increasing **P** content up to 35 mol % gives us the chance of correcting the assignment of $S_{\beta\beta}$ and $S_{\alpha\gamma}$ resonances previously proposed. Indeed, Kimura assigned a resonance appearing, in his spectral conditions ($T = 130$ °C, solvent: *o*-dichlorobenzene/deuteriobenzene-d_6), at 22.27 ppm to carbon $S_{\beta\beta}$, the central methylene carbon of the sequence **PEP** shown in Scheme 3. This resonance, just detectable in the spectrum of the copolymer that contained only 2 mol % comonomer, was noticeably more intense in the spectrum of the ethyl ether soluble fraction that contained 19.4% **P** and was likely produced by the less stereospecific active centers.

Such a resonance is absolutely absent in the complete set of spectra that we have analyzed, even in the spectrum of Figure 1c and d, where, due to the high 4-methyl-1-pentene content, the **PEP** sequence is expected to be relatively frequent. The arrow in spectra (c) and (d) shows the open region in which such resonance should have appeared. On the other hand, we observe a well-separated signal at 24.57 ppm, whose area increases at increasing **P** content and is always about one-half of the area of the broad resonance appearing from 32.5 to 33.0 ppm, assigned to the two necessarily connected $S_{\alpha\gamma}$ methylene carbons of the same **PEP** sequence (Scheme 3).[3]

The signal at 24.57 ppm, which in Kimura's spectrum appears as a low-intensity peak not well resolved from the $S_{\beta}\delta$ signal, was assigned to the $S_{\beta}\delta$-**PPEE** sequence. According to our observations, this signal cannot but be assigned to the $S_{\beta\beta}$ carbon.

However, such an assignment opens some questions. The first regards the chemical shift value that on the basis of simple additive rules should be similar to that of the same sequence in ethylene/hexene and ethylene/octene copolymers (that actually corresponds to Kimura's assignment). Indeed, the Grant and Paul "ϵ" parameter would predict small chemical shift differences among the corresponding $S_{\beta\beta}$ carbons in these three copolymers. In ethylene/higher α-olefin copolymers, the chemical shifts of some of the tetrad and pentad sequences are very

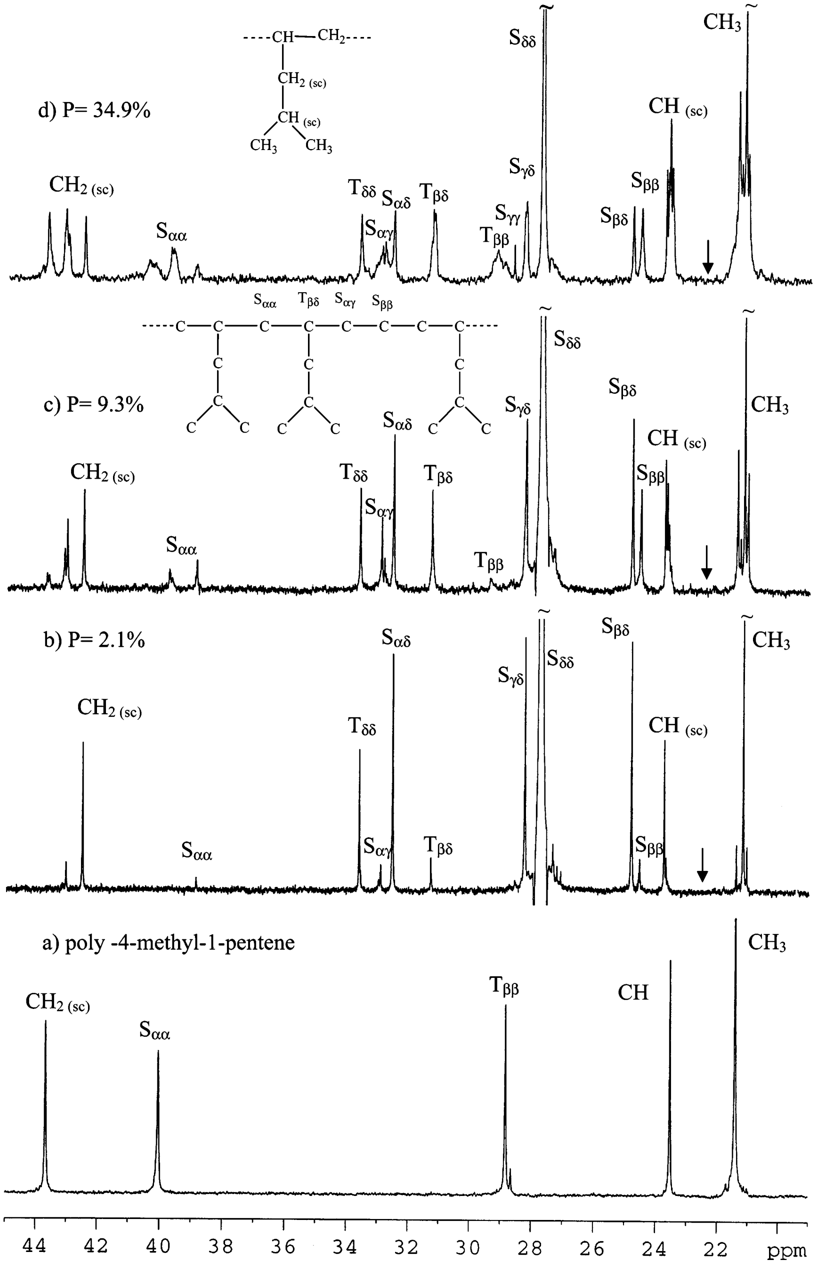
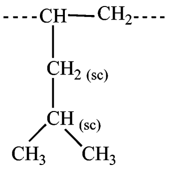


Figure 1. ^{13}C NMR spectra of ethylene-4-methyl-1-pentene copolymers with different comonomer content: (a) poly-4-methyl-1-pentene, (b) 2.1 mol % content (run 2 in Table 1), (c) 9.3 mol % content (run 4 in Table 1), and (d) 34.9 mol % content (run 6 in Table 1).

Scheme 2



slightly affected by branch length for those branches two carbons in length and longer. The chemical shift of $S_{\beta\beta}$ carbon in **E/P** copolymers is more than 2 ppm downfield with respect to the expected value. A second question regards the peak multiplicity. In the spectrum of ethylene/hexene (**E/H**) copolymers, three signals are detected for **EHEHE**, **EHEHH**, and **HHEHH** sequences, respectively.[19] The same is observed for ethylene/octene copolymers.[15] On the contrary, $S_{\beta\beta}$ carbon in **E/P** copolymers gives a single signal at all of the comonomer content (see Figure 1) and seems thus unaffected by any comonomer substitution farther than the PEP sequence. We supposed that conformational analysis computations could account for these differences, probably deriving from the steric hindrance of the branched comonomer unit.[20]

In light of the consideration that the signal at 22.29 ppm was mainly observed by Kimura in the spectrum of a stereoirregular copolymer fraction, we suggest that it could be related to the presence of stereoirregular sequences that in the spectra of Figure 1 are absolutely absent. This point will the object of further investigation performed on **E/P** copolymers prepared with less stereoregular metallocene catalysts.

We can also observe that, differently from carbon $S_{\beta\beta}$, in the multiplet assigned to the $S_{\alpha\gamma}$ methylene carbons, it is possible to distinguish three main signals at 32.99, 32.93, and 32.84 ppm, respectively. By analysis of the intensity variations of these three resonances at increasing **P** concentration (Figure 3), it is easy to assign the upfield signal at 32.84 ppm to the $S_{\alpha\gamma}$ methylene carbons in the sequence **PPEPP** (**21**), the signal at 32.93 ppm to the sequence **PPEPE** (**22**), and the signal at 32.99 ppm to the sequence **EPEPE** (**23**) (see Scheme 4).

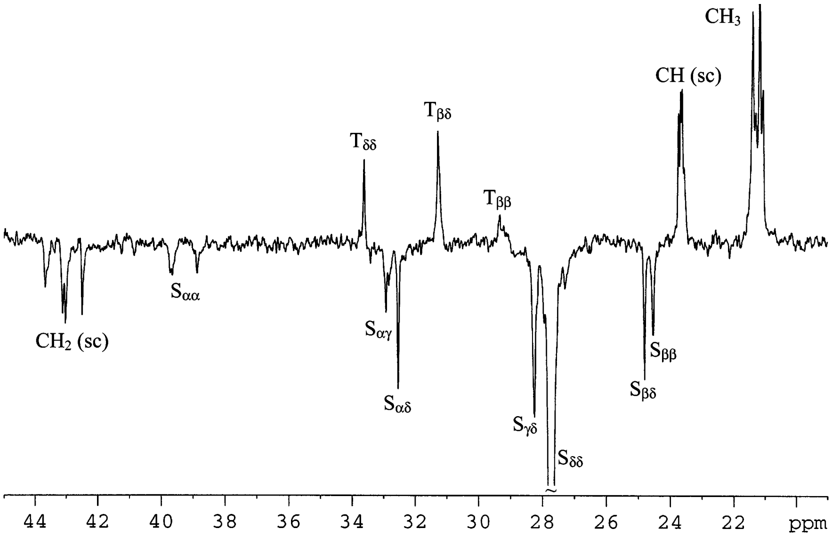


Figure 2. ^{13}C NMR DEPT spectrum of ethylene-4-methyl-1-pentene copolymers with 13.5 mol % comonomer content (run 5 in Table 1).

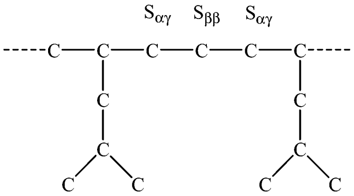
Table 2. ^{13}C NMR Chemical Shift Assignment for Ethylene/4-Methyl-1-pentene Copolymer Obtained with *rac*-CH$_2$(3-^{t}BuInd)$_2$ZrCl$_2$

			shift (ppm)				
			this work			Δδ ^{c} (ppm)	
carbon	sequence[a]	no.	homopolymer	copolymer	lit[b]	this work	lit.[b]
CH$_3$(sc)	EP*P*^{e}E□	**1**		21.06	21.51	−0.12	−0.22
	PP*P*^{e}E□	**2**		21.08		−0.10	−0.22
	E*P*E	**3**		21.18	21.27	0.00	0.00
	PP*P*^{i}E□	**4**		21.30	21.51	0.12	0.22
	EP*P*^{i}E□	**5**		21.40		0.22	0.22
	PP*P*P□	**6**		21.40		0.22	0.22
	EP*P*PE	**7**		21.42	21.57	0.24	0.28
	PP*P*PP		21.41				
CH(sc)	PP*P*PP		23.52			−0.23	−0.14
	EP*P*PE	**8**		23.52	23.92		
	PP*P*P□	**9**		23.57	23.92	−0.18	−0.14
	PP*P*E□	**10**		23.64	24.10	−0.11	−0.04
	EP*P*E□	**11**		23.69		−0.06	−0.04
	E*P*E	**12**		23.75	24.06	0.00	0.00
S$_{\beta\beta}$	PEP	**13**		24.57	**22.27**[d]		
S$_{\beta\delta}$	PEE	**14**		24.81	25.22		
S$_{\delta\delta}$	EEEE	**15**		27.73	27.99		
S$_{\gamma\delta}$	PEEE	**16**		28.23	28.49		
S$_{\gamma\gamma}$	PEEP	**17**		28.65	29.04		
T$_{\beta\beta}$	PPP	**18**	28.82	29.32	29.45		
T$_{\beta\delta}$	PPE	**19**		31.29	31.89		
S$_{\alpha\delta}$	EPEE	**20**		32.54	**32.99**[d]		
	PPEE				**33.48**[d]		
S$_{\alpha\gamma}$	PPEPP	**21**		32.84	**33.93**[d]		
	PPEPE	**22**		32.93			
	EPEPE	**23**		32.99	**33.48**[d]		
T$_{\delta\delta}$	EPE	**24**		33.62	34.08		
S$_{\alpha\alpha}$	EPPE	**25**		38.87	39.39		
S$_{\alpha\alpha}$	EPPPE□	**26**		39.66	40.29		
	PPPPE□	**27**		39.73			
S$_{\alpha\alpha}$	EPPPPE	**28**		40.22	40.83		
	PPPPP□	**29**		40.43			
	PPPPPP		40.03				
CH$_2$(sc)	E*P*E	**30**		42.50	42.89	0.00	0.00
	EP*P*E□	**31**		43.05	43.46	0.55	0.59
	PP*P*E□	**32**		43.12	43.46	0.62	
	EPPPE	**33**		43.60	44.06	1.10	1.25
	PP*P*P□	**34**		43.67	44.06	1.17	
	PP*P*PP		43.66				

[a] □ = E or P. [b] As reported by Kimura et al. for ethylene/4-methyl-1-pentene copolymers.[3] To facilitate the comparison, chemical shifts from literature were referred to internal HMDS [δ(HMDS) = δ(TMS) − 2 ppm]. [c] Chemical shift differences relative to the values of EPE, which are set to be 0 ppm. [d] Assignment modified in the present work.

It is interesting to observe that signal **23**, which we assign to the alternating sequence, is hardly detected even when **P** content is as low as 2.1 mol % and is nearly absent at higher **P** content. This is in agreement with findings reported in the literature according to which the stereorigid, sterically hindered, isospecific metallocene *rac*-H$_2$C−(3-^{t}BuInd)$_2$ZrCl$_2$ promotes ethene/propene copolymers with a relatively high reactivity ratio product (r_1r_2), which arises also and surprisingly from a

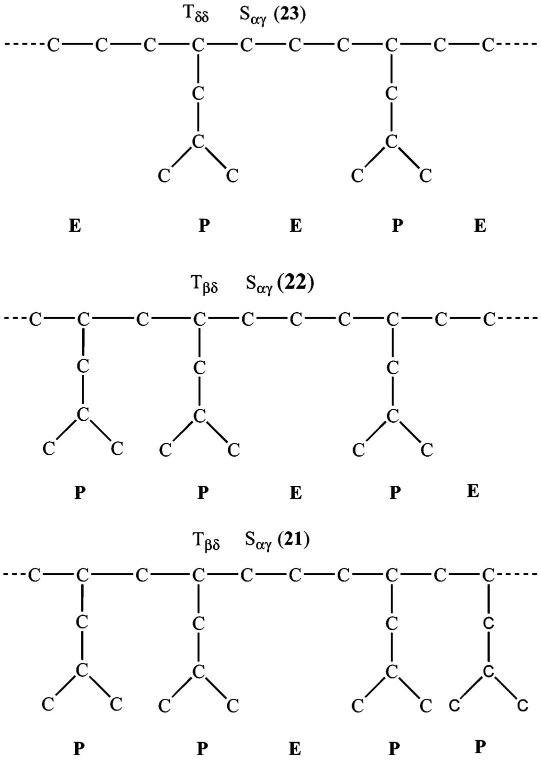
Scheme 3



relatively high r_2 value.[21,22] The capacity of this catalyst of giving **PP** dyads at such low comonomer content is confirmed by the presence of a narrow signal at 31.29 ppm assigned to the $T_{\beta}\delta$ methine carbon, which is well detectable even in the copolymer with 1.2% **P** content. However, for a safer assignment of sequence (**23**), we have analyzed the same spectral region of a sample of **E/P** copolymer containing 4.3 mol % of 4M1P (Figure 4) prepared with *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride [*rac*-EBTHIZrCl$_2$], which promotes ethene/propene copolymers with a relatively low reactivity ratio product ($r_1r_2 = 0.49$).[23] We can observe that signal (**23**) of the alternating sequence **EPEPE** is prevailing here, as expected as a consequence of the low comonomer composition and of the copolymerization statistics of [*rac*-EBTHIZrCl$_2$] catalyst, and can be safely assigned.

We notice that the assignment of these three sequences differs from literature assignment and is in opposite direction from the location predicted by Grant and Paul additivity rules,[24,25] according to which the "δ" contribution leads to a prediction of downfield shift for the more branched sequences. This seems to be one of the cases in which the γ-gauche conformational effect prevails over the constitutive effects.

Scheme 4



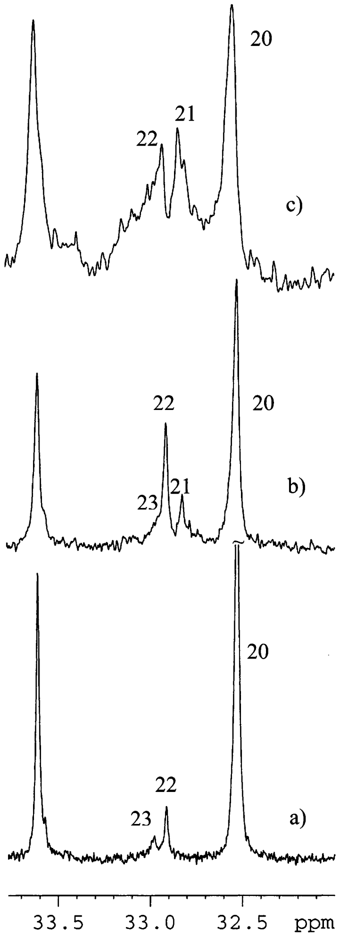


Figure 3. Expanded plot of the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ region of ethylene-4-methyl-1-pentene copolymers with different comonomer content: (a) 2.1 mol % content (run 2 in Table 1), (b) 9.3 mol % content (run 4 in Table 1), and (c) 34.9 mol % content (run 6 in Table 1).

The assignment of the $S_{\alpha\delta}$ methylene carbon also differs from the literature assignment. Indeed, two different $S_{\alpha\delta}$ signals would have been expected for **EPEE** and **PPEE** sequences. Two signals were in fact assigned by Kimura to $S_{\alpha\delta}$ carbon, the $\alpha\delta$-**PPEE** sequence being supposed to be unresolved from the $\alpha\gamma$-**EPEPE** sequence, the sum of the carbon effects being the same in both cases. (Scheme 5).

On the contrary, we have detected a single signal at 32.54 ppm, which is narrow in spectra of Figure 1b and c and becomes much broader in spectrum of Figure 1d, at higher comonomer content. This could reflect a slight chemical shift inequivalence of **EPEE** and **PPEE** sequences.

The assignment of all the other carbons of the main chain closely agrees with the data from literature, the small differences (less than 0.5 ppm) likely deriving from the different spectral conditions. Thus, they do not deserve any further discussion.

It seems to us worthwhile to underline that, thanks to this careful analysis of a suitable series of copolymers only differing in comonomer content, we can propose a correct assignment

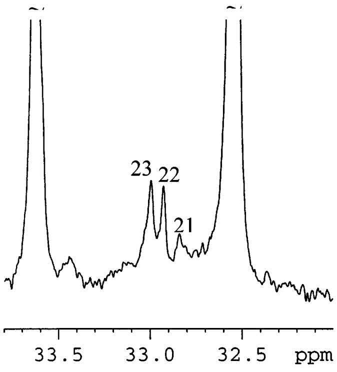
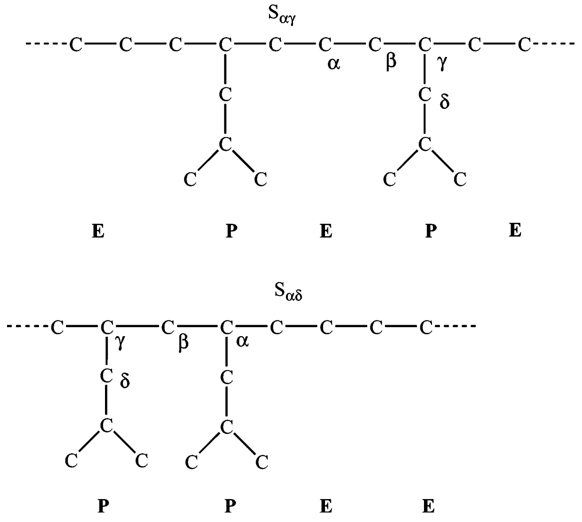


Figure 4. Expanded plot of the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ region of ethylene-4-methyl-1-pentene copolymer prepared with (r-EBTHIZrCl$_2$)/MAO catalyst.

Scheme 5



of $S_{\beta\beta}$, $S_{\alpha\gamma}$, and $S_{\alpha\delta}$ methylene carbons. This will permit a precise measurement of the entire set of methylene peak areas present in the copolymers studied in this paper and, consequently, a correct determination of dyad and triad copolymer composition and of comonomer content and distribution.

The composition of the copolymers presented in this paper was calculated from the dyad distribution using methylene peaks $S_{\alpha\alpha}$, $S_{\alpha\gamma}$, $S_{\alpha\delta}$, $S_{\delta\delta}$, $S_{\beta\delta}$, and $S_{\gamma\delta}$, following ref 26 and from triad distribution in two different ways: (i) using methylene side chain CH_2(sc) and main chain methylene peaks $S_{\beta\beta}$, $S_{\delta\delta}$, $S_{\beta\delta}$, and $S_{\gamma\delta}$ and (ii) using methine peaks ($T_{\beta\beta}$, $T_{\beta\delta}$, and $T_{\delta\delta}$) and main chain methylene peaks, $S_{\beta\beta}$, $S_{\delta\delta}$, $S_{\beta\delta}$, and $S_{\gamma\delta}$.[27] The good agreement among the results obtained from the three methods supports the correctness of the set of assignments that we have proposed (see Supporting Information).

Side Chain Region. Figures 5, 6, and 7 show the expanded plots of the spectral regions of methylene CH_2(sc), methine CH(sc), and methyl carbons of the side chain for three comonomer compositions (2.1, 9.3, and 34.9%, respectively, in mol). The spectral region relative to methylene CH_2(sc) is very well resolved and can be the basis for the assignments of the other spectral regions. Thus, we will comment on this region first.

Methylene CH_2(sc) Region. The resonances of CH_2(sc) (Figure 5) can be easily explained in terms of mainly additive effects arising from substitution of **E** with **P** at one or both sides of the observed carbon. If the signal at 42.50 ppm, assigned to **EPE** (**30**) triad in the copolymer containing the lowest comonomer amount (Figure 5a), is taken as the reference chemical shift, the first substitution of **E** with **P** on one side gives a lower field shift of the observed CH_2(sc) to 43.05−43.12 ppm (**PPE** centered sequences), while the same substitution on the other side gives a further downfield shift to 43.60−43.67 ppm (**PPP** centered sequences) (see Figure 5b and c). Thus, the three **P** centered triads, **PPP**, **PPE**, and **EPE**, are definitively assigned and very easily evaluated.

By inspection of the intensity variation of the resonances at different comonomer composition, we can assign sequences longer than triads. In the spectrum of the copolymer containing the lowest comonomer amount (Figure 5a), it is easy to assign the **PPE** centered pentad richest in ethylene **EPPEE** (**31**) at 43.05 ppm. Because the introduction of **E** on one side decreases or cancels the effect of further substitution on the same side (indeed, the **EPE** sequence is always observed as a narrow single peak), **EPPEE** and **EPPEP** pentads (both of them likely present at higher **P** content) are actually indistinguishable, thus we indicate them as **EPPE□**. From now on, symbol □ means **P** or **E** in all pairs of sequences which are indistinguishable for the said reason. By observing the resonance intensity variation at increasing **P** content in the spectra of Figure 5b and c, the **PPPE□** (**32**) sequence is assigned at 43.12 ppm. In spectra (b) and (c), we can also assign the **EPPPE** (**33**) pentad at 43.60 ppm and the PPPPE pentad (**34**) at 43.67 ppm. This pentad is indistinct from the signal of CH_2(sc) in the homopolymer.

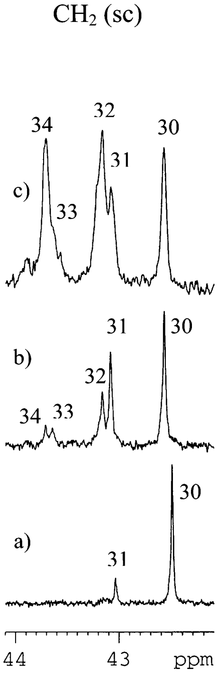


Figure 5. Expanded plot of the methylene side chain region, CH_2(sc), of ethylene-4-methyl-1-pentene copolymers with different comonomer content: (a) 2.1 mol % content (run 2 in Table 1), (b) 9.3 mol % content (run 4 in Table 1), and (c) 34.9 mol % content (run 6 in Table 1).

Methine CH(sc) Region. As is apparent by inspection of the spectra of Figure 6, the CH(sc) region is less resolved than the methylene CH_2(sc) region and consequently is less suitable for quantitative evaluation of **P** centered sequences. However, by analysis of the intensity peak, variations among the copolymers with increasing **P** content, and especially by comparison with the intensities of the more resolved signals of the corresponding CH_2(sc) region (Figure 5), it is possible to unequivocally assign the resonances **8**−**12**, as shown in Figure 5 and in Table 2. In particular, resonances **8** and **9** are unexpectedly assigned to **EPPPE** and **PPPPE** sequences, respectively, by comparison with the areas of the signals **33** and **34** safely assigned to the same sequences.

Methyl Region. The methyl region (Figure 7) presents a more complicated pattern. Here, the comparison with the corresponding spectral regions relative to CH_2(sc) of Figure 5 is fundamental for the assignment. Taking the signal of the **EPE** sequence (**3**) at 21.18 ppm as a reference, in the copolymer containing the lowest comonomer amount (Figure 7a), we observe the presence of two small resonances of similar intensities, **1** and **5**, at higher (21.06 ppm) and lower (21.40 ppm) field with respect to **EPE**. In the corresponding spectrum of Figure 5a, besides the **EPE** resonance, only one signal (**31**) is detected, that was unequivocally assigned to the **EPPE□** sequence. The integrated peak area of signal **31** is about one-half the sum of the areas of resonances **1** and **5**. Therefore, both resonances **1** and **5** should be related to **EPPE□** sequence. Taking into account that one of the two resonances (**5**) is actually

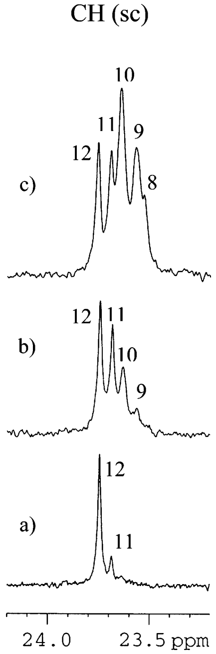


Figure 6. Expanded plot of the methine side chain region, CH(sc), of ethylene-4-methyl-1-pentene copolymers with different comonomer content: (a) 2.1 mol % content (run 2 in Table 1), (b) 9.3 mol % content (run 4 in Table 1), and (c) 34.9% content (run 6 in Table 1).

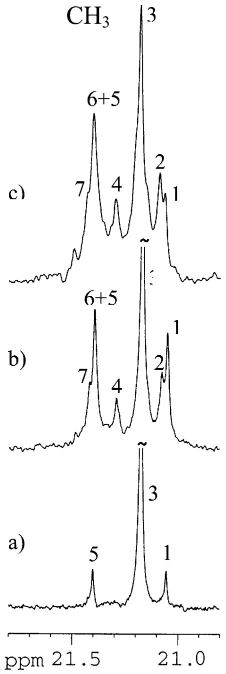
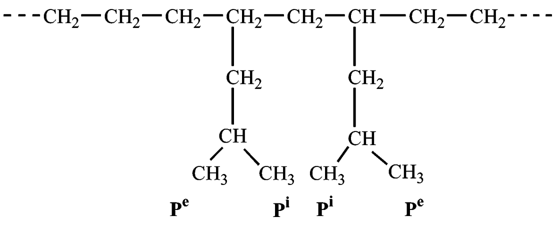


Figure 7. Expanded plot of the methyl side chain region, CH_3, of ethylene-4-methyl-1-pentene copolymers with different comonomer content: (a) 2.1 mol % content (run 2 in Table 1), (b) 9.3 mol % content (run 4 in Table 1), and (c) 34.9 mol % content (run 6 in Table 1).

coincident with the methyl resonance of 4-methyl-1-pentene homopolymer, we assign this resonance to the more shielded "internal" methyl carbon of the **PP** dyad in **EPPEE** sequence. Consequently, resonance **1** cannot but be assigned to the less shielded "external" methyl carbon of the **PP** sequence, the one next to the **E** unit. From now on we will distinguish the two different methyls as $\mathbf{P}^i$ (internal) and $\mathbf{P}^e$ (external).

Scheme 6, which represents the structure of a **EPPE** sequence, shows that the methyls indicated as $\mathbf{P}^i$ are diastereotopic with respect to the methyls indicated as $\mathbf{P}^e$. Thus,

Scheme 6



depending on differences in γ-gauche conformations, they have different average shielding effects, resulting in different chemical shifts. The nonequivalence of the methyl carbons is also observed for the four crystalline forms of the isotactic poly-4-methyl-1-pentene that have been studied through solid-state ^{13}C NMR CP-MAS spectroscopy. This has been explained on the basis of the γ-gauche shielding interaction and of the conformations of polymer chains and lateral groups.[28]

At increasing **P** concentration, two other resonances appear, still at higher and lower field with respect to the reference **EPE** sequence, at 21.08 (**2**) and 21.30 (**4**) ppm, respectively. On the basis of analogous considerations as above, we assign resonance **4** to the "internal" and resonance **2** to the "external" methyl carbon of **PPPEE** pentad. The two pentads **EPPEE** and **PPPEE** do not appear distinguishable from **EPPEP** and **PPPEP**, respectively. Thus, we indicate the two pairs of pentads in Table 2 as **EPPE□** and **PPPE□**.

In Figure 7b, we also observe that signals **1** and **5**, which in the spectrum of Figure 7a have the same intensity, appear slightly unbalanced, signal **5** appearing more intense than signal **1**. This effect becomes much more evident in Figure 7c. Our hypothesis is that the signal of **PPPP□** (**6**) pentad is unresolved from that of $\mathbf{EPP^iE□}$. Such a hypothesis is supported by the comparison of the integrated peak areas of signals **1** and **5** of Figure 7b and signal **34** of the corresponding Figure 5b. Indeed, the area of signal **34** (assigned to **PPPP□** pentad) is about one-half the difference between the areas of signals **1** and **5** (from now on **6** + **5**).

A resonance (**7**), poorly resolved from signal **6** + **5**, is also detected in Figure 7b and c at 21.42 ppm. This resonance is assigned to the **EPPPE** pentad by comparison with the integrated peak areas of the corresponding methyne (**8**) and methylene (**33**) peaks.

Because of the overlapping of several sequences in the three spectral regions of methylene CH_2(sc), methine CH(sc), and methyl carbons and to the general phenomenon that after an **E** substitution, the effect of further substitution is undetected; although many **P** centered pentad signals have been definitively assigned, a quantitative evaluation of only a few pentads is actually possible through the simple analysis of this spectral region unless probabilistic considerations are introduced.

Experimental Section

General Remarks. Manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques or in a drybox under nitrogen atmosphere (<10 ppm oxygen, <20 ppm water). Toluene was dried by distillation from sodium under nitrogen atmosphere. Methylaluminoxane (MAO) (Witco, 10 wt % solution in toluene) was used after drying in a vacuum to remove the solvent and unreacted trimethylaluminum (TMA) and was stored under nitrogen. [*rac*-H_2C-(3-^{t}BuInd)$_2$$ZrCl_2$] was used as kindly donated by L. Resconi; [*rac*-(EBTHI)$ZrCl_2$] was provided by Basell Poliolefine Italia S.r.l. Nitrogen and ethene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4 Å molecular sieves.

Ethene/4-Methyl-1-pentene Polymerizations. In a typical polymerization reaction, a 0.25 L Büchi autoclave equipped with a mechanical stirrer was charged under nitrogen with a solution of the proper amount t of 4-methyl-1-pentene, 7.5 mmol of dry methylaluminoxane (MAO) in 100 mL of anhydrous toluene. A 25 mL injector was charged with 10 mL of a solution of 10 μmol of catalyst (*rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl$_2$ or *rac*-(EBTHI)ZrCl$_2$) and 2.5 mmol of MAO in toluene (total MAO/Mt ratio = 1000). After thermal equilibration of the reactor system at 45 °C, ethene was continuously added until saturation. When the equilibrium pressure (2.47 atm) was reached, the injector with the metallocene solution was pressurized with nitrogen, and the solution was injected into the reactor. The reaction was terminated by addition of a small amount of ethanol, and the polymer was precipitated upon pouring the whole reaction mixture into ethanol (500 mL) to which concentrated hydrochloric acid (5 mL) had been added. The polymer was collected by filtration and dried under vacuum at 70 °C.

Nuclear Magnetic Resonance (NMR). ^{13}C NMR spectra of the polymers were recorded in $CDCl_2CDCL_2$ at 103 °C on a Bruker AM-400 spectrometer operating at 100.58 MHz, (internal chemical shift reference: 1% hexamethyldisiloxane). Conditions: 10 mm probe, 90° pulse angle, 64 K data points, acquisition time 5.56 s, relaxation delay 20 s, 3−4 K transients. Proton broadband decoupling was achieved with a 1D sequence using bi_waltz16_32 power-gated decoupling.

^{13}C DEPT NMR spectra were measured with composite pulse decoupling using the sequence τ 1−90°−τ_2−180°, 90°−τ_2−135°, 180°−τ_2−CPD−acquire, with delays τ_1 of 5 s, and τ_2 of 3.8 ms, and 90° pulse widths of 14.3 and 28.1 μs and for ^{13}C and ^{1}H, respectively.

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Supporting Information Available: Composition of run 5 of Table 1 calculated from the dyad and triad comonomer distribution on the basis of the signal assignments proposed in the present paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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