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ARTICLE

Ethene/4-Methyl-1-pentene Copolymers by Metallocene-Based Catalysts: Exhaustive Microstructural Characterization by ^{13}C NMR Spectroscopy

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ABSTRACT: The availability of a series of ethene/4-methyl-1-pentene copolymers spreading over a very broad range of chemical compositions, from about 1% up to 90% as 4-methyl-1-pentene molar content, paralleled by the heteronuclear ^{1}H−^{13}C gradient-assisted 2D NMR techniques, has allowed for an improved peak assignment of their ^{13}C NMR spectra. In particular, sequences richer in comonomer could be assigned, and the previous ambiguous assignment of $S_{\alpha\gamma}$ methylene carbon of the main chain was corrected. Starting from whole set of the previous and newly proposed assignments, a comprehensive check of consistency of the ^{13}C NMR assignment can be completely fulfilled. From now on, the correct evaluation of the copolymer microstructure at tetrad level and of the copolymerization parameters of this interesting family of copolymers will be accessible.

Introduction

Ethene/4-methyl-1-pentene (E/4M1P) copolymers have been considered an interesting family of materials since the early 1970s, for the properties of the polymers can be significantly influenced by incorporation of small amount of sterically hindered olefins. Indeed, the bulky branched substituent is expected to lower density of polyethene more effectively than linear α-olefins (e.g., 1-butene, 1-hexene, and 1-octene) at a similar level of incorporation.[1] The limitation to their large-scale application was mainly due to the fact that the heterogeneous Ziegler−Natta catalysts originally used for the copolymerization led to a low incorporation of the α-olefin (no more than 2−3 mol %) in the polyethene chain as well as to a broad intermolecular distribution of molecular mass and chemical composition.

The development of the so-called single-site catalysts has paved the way for the production of copolymers with homogeneous comonomer distribution, along with controlled comonomer content, even when nonconventional bulky and/or branched comonomers, such as 4M1P, were used. The chance of modulating polymer molecular features, through the control of content and intramolecular distribution of branching, could be in principle applied to obtain target values of thermal and mechanical properties as well as of polymer density and free volume.

The composition of the copolymer as well as its sequence distribution significantly affects the material properties of the product. They also reveal details about the polymerization chemistry. ^{13}C NMR has been the most successful analytical tool used to characterize ethene-based copolymers in order to evaluate composition and sequence distribution.[2] Correct and unambiguous peak assignment is the starting point of all quantitative NMR analysis.

During the 1980s and 1990s the microstructural characterization of E/4M1P copolymers was performed following a pioneering ^{13}C NMR assignment by Kimura et al.,[3] mainly based on the analysis of a copolymer obtained with a traditional Ziegler−Natta catalyst, containing about 2 mol % of comonomer. Of course, only a restricted number of copolymer sequences could be detected in the copolymers studied by these authors, several assignments being based on calculations. Recently, we reported on a wide ^{13}C NMR assignment of E/4M1P copolymers obtained with the stereorigid and sterically hindered metallocene catalyst *rac*-[methylenebis(3-*tert*-butyl-1-indenyl)]zirconium dichloride (*rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl$_2$) (**TBI**).[4] This highly isoselective and completely regioselective catalyst[5] has been extremely useful for this kind of research, since it produces a copolymer where the spectral multiplicity can only be ascribed to differences in comonomer sequences. Moreover, **TBI** is able to promote ethene/4M1P copolymerization with a quite high reactivity ratio product ($r_1r_2 = 17.2$),[6] with relatively high values of both r_1 and r_2.

The occurrence of long comonomer sequences and the unusual absence of alternating comonomer sequences result in a further simplification of the spectral pattern and allow for a more in-depth assignment of a few particular spectral regions.

More recently, we could enlarge the series of E/4M1P copolymers from **TBI** to higher comonomer contents: for the first time, E/4M1P copolymers are available in a very broad range of chemical compositions, from about 1% to 90% as 4M1P molar content. The access to new copolymer compositions has allowed us to achieve a more detailed assignment of the sequences richer in comonomer: in particular, the previously ambiguous assignment of $S_{\alpha\gamma}$ and $S_{\gamma\delta}$ methylene carbons could be noticeably improved.

The new assignments were made possible through the application of the two-dimensional heteronuclear (^{1}H−^{13}C) correlation measurements on selected samples. The E/4M1P microstructure was explored applying the gradient-assisted 2D NMR techniques such as g-HSQC (heteronuclear single quantum coherence) and g-HMBC (heteronuclear multiple bond correlation), at high temperature, with the aim of increasing the molecular mobility[7,8] and thus obtaining sharper resonances.

In light of all previous and new findings, we can here propose a refined, complete, and unambiguous set of resonance assignments that completely fulfill a comprehensive check of consistency among the integrals from peaks belonging to the same microstructure.

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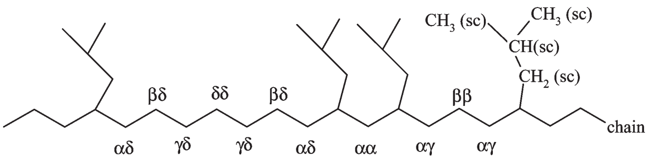
Table 1. Ethene/4-Methyl-1-pentene Copolymerization from *rac*-H_2C-(3-^{t}Bu-Ind)$_2ZrCl_2$ and MAO as the Catalytic System[a]

run	f^b (mol/mol)	yield (g)	t_{pol} (min)	activity × 10^{-3} ($mg_{pol}/mmol_{Mt} \times h$)	4M1P[c] (mol %)	M_w	M_w/M_n	monomer conversion (%)
1[e]	1.883	0.659	30	791	1.18	n.d.[f]	n.d.[f]	1.7
2[e]	0.932	0.370	30	888	2.76	n.d.[f]	n.d.[f]	0.9
3[e]	0.457	0.680	15	136	5.19	n.d.[f]	n.d.[f]	1.8
4[e]	0.224	0.338	30	68	8.49	n.d.[f]	n.d.[f]	0.8
5	0.264	1.000	6	3300	15.01	65 660	2.2	9.3
6	0.126	1.100	10	2178	23.66	68 440	2.3	8.1
7	0.082	0.958	12	1581	33.44	n.d.[f]	n.d.[f]	5.9
8	0.054	1.726	20	1709	55.08	26 960	2.6	9.6
9	0.028	0.270	40	23	57.26	39 300	2.6	0.9
10	0.025	0.687	40	340	60.92	78 900	2.6	2.1
11	0.022	4.158	55	898	74.76	59 140	2.5	12.8
12	0.015	2.653	50	631	85.83	78 780	2.3	6.4

[a] Polymerization conditions: total volume = 100 mL, [catalyst] = 3 at 10 μmol, Al/Mt = 1000 at 3000 (mol/mol), $T = 45$ °C, $P = 1$ atm. [b] E/4M1P feed ratio (mol/mol) in liquid phase. [c] From ^{13}C NMR analysis. [d] Molecular weight from GPC analysis. [e] Cited from ref 11. [f] n.d. = not determined.

Scheme 1



A route for achieving complete and detailed structural information on this promising family of copolymers is thus available.

Results and Discussion

A general structure of E/4M1P copolymer is shown in Scheme 1. The carbon terminology follows that of Carman and Wilkes,[9] where P, S, and T, refer to the primary (methyl), secondary (methylene), and tertiary (methine) carbons of the main chain, respectively. Methylene carbons along the backbone are identified by a pair of Greek letters to indicate the distances of the carbon from the neighboring methines. Methyl, methylene, and methine carbons in the side chain are designated by the symbols CH_3(sc), CH_2(sc), and CH(sc).

Refinement of Previous αγ Methylene Assignment. In recent publications, we have proposed what is so far, at the best of our knowledge, the most detailed ^{13}C NMR assignment on E/4M1P copolymers.[4,10,11] The assignment had been carried out on a relatively limited set of experiments, the comonomer content spanning from about 1 to about 30 mol %. The range of composition was recently enriched with numerous further experiments: thus, now we can fund our studies on a quite complete series of copolymers, the range of chemical composition expanding even to 90% as 4M1P molar content (see Table 1).

The newly collected data have focused our attention on the ambiguous assignment of a few methylene carbons of the main chain, whose incorrect evaluation could compromise the determination of the comonomer content and of the copolymerization parameters. Indeed, after applying the quantitative self-consistency check,[11] which is defined as the agreement among the integrals from peaks assigned to the same microstructure, to the spectra of the novel copolymers richer in comonomer, we had concerns about a few particular assignments, namely those of the methylenes $S_{\gamma\delta}$ and $S_{\alpha\gamma}$.

Figure 1 shows the ^{13}C NMR spectra of a series of E/4M1P copolymers with increasing comonomer content. At low comonomer content, when isolated comonomer units are mainly present, αδ, βδ, and γδ resonances from the main chain are expected to have almost the same amplitude, as belonging to the same PEEE sequence (Scheme 2). At increasing comonomer content, another relationship connects αδ, βδ, and γγ, due to the presence of the PEEP tetrad, as shown in Scheme 3.

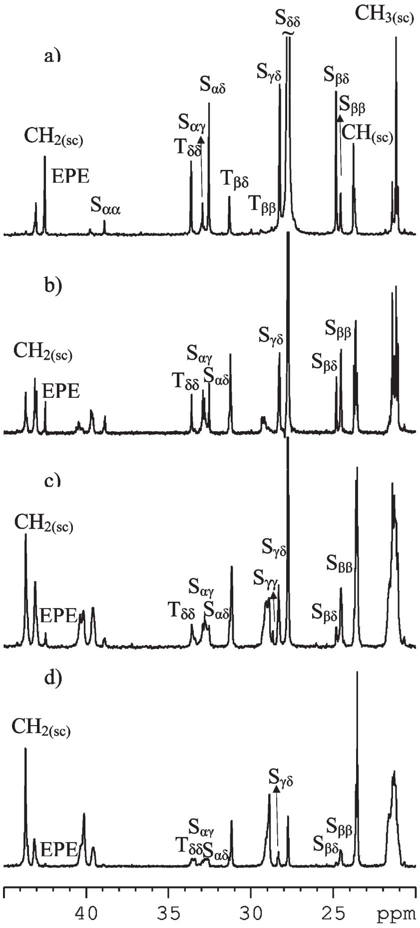


Figure 1. ^{13}C NMR spectra of E/4M1P copolymers with different comonomer content: (a) 5.19 mol % (run 3 in Table 1), (b) 23.66 mol % (run 6 in Table 1), (c) 55.08 mol % (run 8 in Table 1), (d) 85.83 mol % (run 12 in Table 1).

In other words, the general eq 1 links the integrals of αδ, βδ, γδ, and γγ methylene carbons of the main chain.

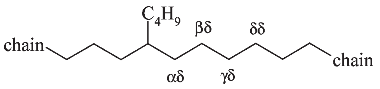
$$S_{\alpha\delta} = S_{\beta\delta} = S_{\gamma\delta} + 2S_{\gamma\gamma} \qquad (1)$$

Equation 1, at low comonomer content, gets into the simpler eq 2.

$$S_{\alpha\delta} = S_{\beta\delta} = S_{\gamma\delta} \qquad (2)$$

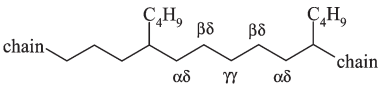
Thus, the integrated peak area of $S_{\gamma\delta}$ is expected to be, in any case, smaller than or equal to those of the $S_{\alpha\delta}$ and $S_{\beta\delta}$

Scheme 2



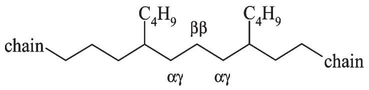
$S_{\alpha\delta} = S_{\beta\delta} = S_{\gamma\delta}$

Scheme 3



$S_{\alpha\delta} = S_{\beta\delta} = 2\ S_{\gamma\gamma}$

Scheme 4



$S_{\alpha\gamma} = 2\ S_{\beta\beta}$

methylene peaks. Indeed, in the spectrum of the copolymer of Figure 1a containing 2 mol % of 4M1P, the integrals of $\alpha\delta$, $\beta\delta$, and $\gamma\delta$ methylenes peaks appear nearly equal within the experimental error. However, in the spectra of the copolymers with higher comonomer content (Figure 1b−d), the integral of the $\gamma\delta$ methylene peak appears surprisingly higher than the other two, and the higher the content, the more evident the effect.

Moreover, another necessary relationship between the integrals of methylenes belonging to the same sequence is not fulfilled. The $\alpha\gamma$ methylene carbon is only present in the PEP triad (Scheme 4) together with the $\beta\beta$ methylene carbon. One $\beta\beta$ methylene carbon, having a chemical shift well established at 24.57 ppm, is associated with two $\alpha\gamma$ methylene carbons; hence, its integral can be used to check the assignment of the $\alpha\gamma$ methylene carbons.[13]

Unexpectedly, the integral of the "assigned" $\alpha\gamma$ methylene in the region between 32.65 and 33.56 ppm is nearly equal to the integral of the $\beta\beta$ methylene at 24.57 ppm (see for instance Figure 1a). On the basis of such observations, it seems likely that the $\alpha\gamma$ carbon should give more than one signal depending on the neighboring comonomer sequences and that one of the possible signals could fall very close to the signal of the $S_{\gamma\delta}$ carbon assigned at 28.23 ppm. Considering the blocky nature of the copolymers produced with **TBI** catalyst and the observed frequency in such copolymers of single ethylene units spanning comonomer homosequences, our hypothesis is that this signal corresponds to the $S_{\alpha\gamma}$ carbon in the PPEPP pentad.

The above hypothesis is supported by 2D NMR experiments (Figure 2) conducted on the E/4M1P copolymer containing 23.66 mol % of comonomer.

The long-range $^1H-^{13}C$ connectivities (Figure 2b) were analyzed with the aim of detecting whether (a) the two carbon atoms $S_{\alpha\gamma}$ in a PPEPP sequence and $S_{\gamma\delta}$ in a PEEE sequence are merging and (b) the resonance for $S_{\alpha\gamma}$ (PPEPP) is different from that of $S_{\alpha\gamma}$ (EPEP□). As shown in the HSQC spectrum in Figure 2a, showing all the direct $^1H-^{13}C$ connectivities, it is evident that the greatest part of the CH_2 protons are in a very crowded spectral region; thus, it was much more significant to extract single rows from the 2D spectrum at the hypothesized ^{13}C chemical shifts of $S_{\alpha\gamma}$ (EPEP□, $\delta c = 32.80$ ppm) and $S_{\gamma\delta}$ (PEEE, $\delta c = 28.23$ ppm). Figure 3a shows the ^1H spectrum corresponding to the row at 32.80 ppm and all the two- and three-bond $^1H-^{13}C$ correlations expected for $S_{\alpha\gamma}$ in a EPEP□ sequences, from now on □ means P or E in all pair of sequences which are indistinguishable; Figure 3b shows the ^1H spectrum corresponding to the row at 28.23 ppm and all the correlations expected for $S_{\gamma\delta}$ in a PEEE sequence. In addition, the correlations of $S_{\alpha\gamma}$ in a PPEPP sequence are observed, confirming that the signal at 28.23 ppm consists of two contributions: one for $S_{\alpha\gamma}$ and the other one for $S_{\gamma\delta}$. Nevertheless, by taking into account this additional $S_{\alpha\gamma}$ contribution, the quantitative self-consistency check is not completely fulfilled.

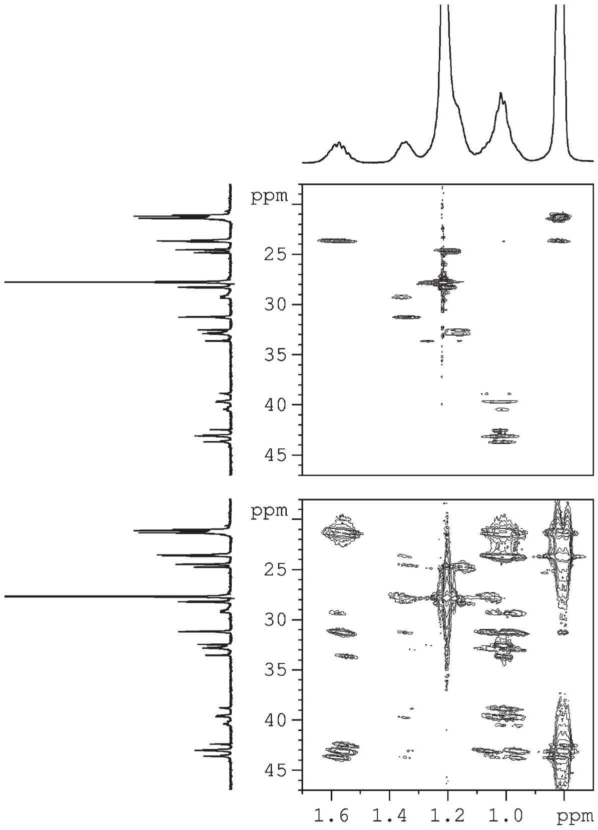


Figure 2. Heteronuclear $^1H-^{13}C$ spectra of E/4MP1 copolymer having 23.66 mol % of comonomer content (run 6 in Table 1): (a) g-HSQC and (b) g-HMBC.

The quantitative self-consistency check shows a further ambiguous assignment. The $\delta\delta$ methine carbon in the EPE sequence was assigned at 33.62 ppm.[4] In principle, the integral of this peak must be equal to that of the side-chain methylene CH_2(sc) of the same sequence, assigned at 42.50 ppm. However, in the spectra of Figure 1c,d, the area of CH_2(sc) appears quite smaller than that of the necessary connected area of the $T_{\delta\delta}$ carbon. Likely, another resonance should overlap the $T_{\delta\delta}$ signal. To corroborate such a hypothesis, a DEPT experiment (Figure 4) was acquired on the same sample containing 23.66 mol % of E/4M1P. Indeed, the DEPT experiment put in evidence the resonance of a secondary carbon at 33.49 ppm (negative peak against positive peaks for tertiary carbons), which is not singled out in any of the spectra of Figure 1, as merging with the signal of the $T_{\delta\delta}$ carbon.

We propose to assign this peak to a further resonance of the $S_{\alpha\gamma}$ carbon. According to this hypothesis, the resonances of $S_{\alpha\gamma}$ methylene in EPEP□ sequences would span from 32.65 to 33.62 ppm. Indeed, the HSQC spectrum (Figure 2a) shows two ^1H resonance peaks for the ^{13}C resonance at 33.62 ppm so validating the last $S_{\alpha\gamma}$ assignment. The former peak, centered at 1.273 ppm, was assigned to a proton directly bonded to the $T_{\delta\delta}$ carbon, while the

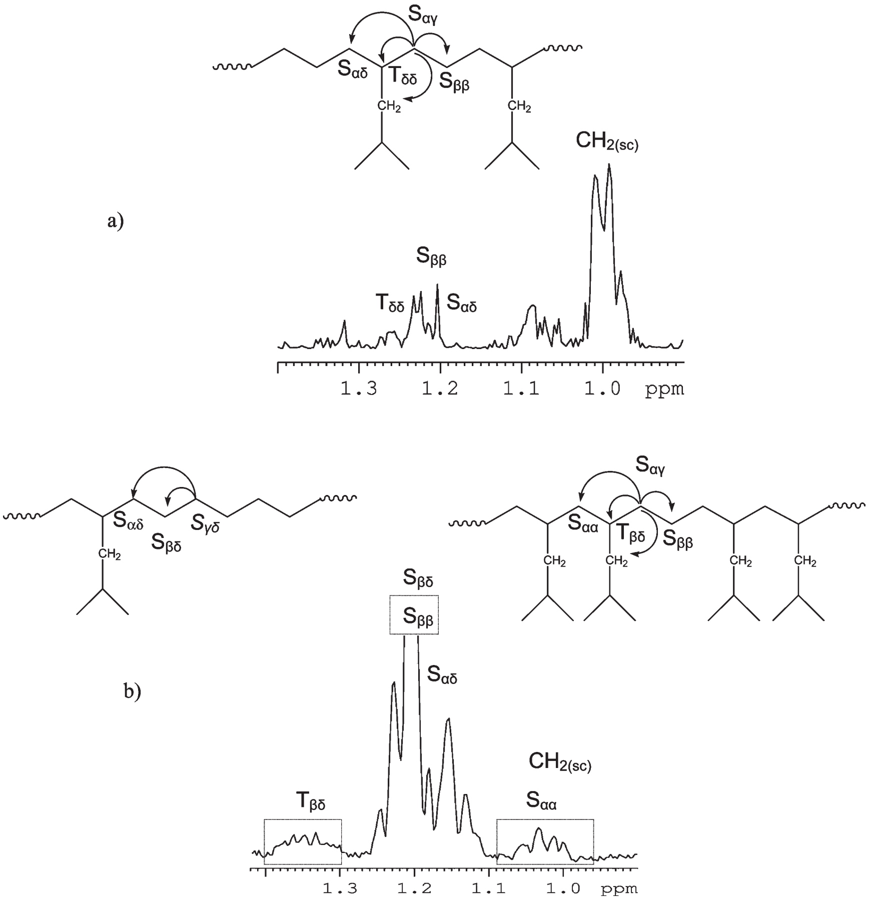


Figure 3. ^{1}H spectra extracted from the HMBC spectrum of Figure 2b, correspondent to row (^{13}C range) at 32.80 ppm (a) and row at 28.23 ppm (b).

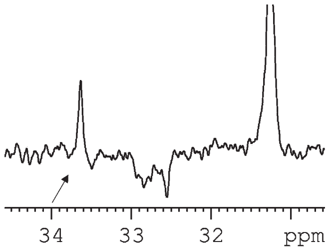


Figure 4. Expanded plot of ^{13}C NMR DEPT spectrum of E/4M1P copolymer with 23.66 mol % comonomer content (run 6 in Table 1).

second one, centered at 1.157 ppm, was compatible with protons bonded to a secondary carbon atom and specifically $S_{\alpha\gamma}$ protons, confirming that $S_{\alpha\gamma}$ and $T_{\delta\delta}$ resonances overlap.

On the basis of the above proposed assignments, a good agreement is now observed between the integrals of the $S_{\alpha\gamma}$ and $S_{\beta\beta}$ carbons belonging to the same sequence (eq 3). The integrated peak areas of the newly assigned resonances are recorded in the spectrum of Figure 5.

$$S_{\alpha\gamma} = 2\cdot S_{\beta\beta} \qquad (3)$$

The $\beta\beta$ carbon is present as a single signal at 24.57 ppm, which is easily measured. The $\alpha\gamma$ carbon is present as a multiplicity of signals that are not directly measurable as merging with others. Therefore, the total $\alpha\gamma$ integral is calculated as the sum of the following contributions: (i) the area of $S_{\gamma\delta} + S_{\alpha\gamma}$ peaks ranging from 28.44 to 28.17 ppm after subtraction of the peak area at 32.54 ppm assigned to $S_{\alpha\delta}$ carbon ($S_{\alpha\delta} = S_{\gamma\delta}$ according to eq 2) plus (ii) the area of the entire region between 32.65 and 33.62 ppm after subtraction of the peak area corresponding to CH_2(sc) in EPE triad at 42.50 ppm (necessarily equal to $T_{\delta\delta}$ in the same EPE triad).

Table 2 lists the signals of the carbons utilized to verify eq 3 along with the corresponding integrals. From Table 2, $S_{\alpha\gamma} = 1 - 2 + 3 + 4 - 5 = 3.971$. From eq 3 and from Table 2, $S_{\alpha\gamma} = 6\ 2 = 2.008 \times 2 = 4.016$. The good agreement between the two obtained values supports the correctness of the proposed assignments.

Signals Improvement. In this section we also propose a refined ^{13}C assignment for E/4M1P copolymers. This improvement was obtained by analyzing the previous data in the light of the new systematic self-consistent approach and fundamental 2D gradient-assisted techniques. Specifically, we were able to identify and justify more than one signal for the $T_{\beta\beta}$ carbons, depending on the block length and comonomer sequences.

As well-known, the $T_{\beta\beta}$ carbon correlates through two bonds, with $S_{\alpha\alpha}$ and $CH_{2(sc)}$ protons and through three bonds with protons $CH_{(sc)}$ and $T_{\beta\delta}$. Consequently, $S_{\alpha\alpha}$ correlations can be considered as starting point for the new backward $T_{\beta\beta}$ check.

As reported in our precedent publications,[4,10] three main resonances have been recognized for $S_{\alpha\alpha}$ depending on the comonomer sequences and on the block length. In details, the assignment can be summarized as follows as follow:

(i) The $S_{\alpha\alpha(1)}$ group, centered at 38.87 ppm, referred to an EPPE sequence; (ii) the $S_{\alpha\alpha(2)}$ group at 39.67−39.73 ppm, referred to EPPPE☐ and PPPPE☐ sequences; (iii) th $S_{\alpha\alpha(3)}$ group centered at 40.43 ppm, referred to longest P sequences, e.g., PPPPP☐.

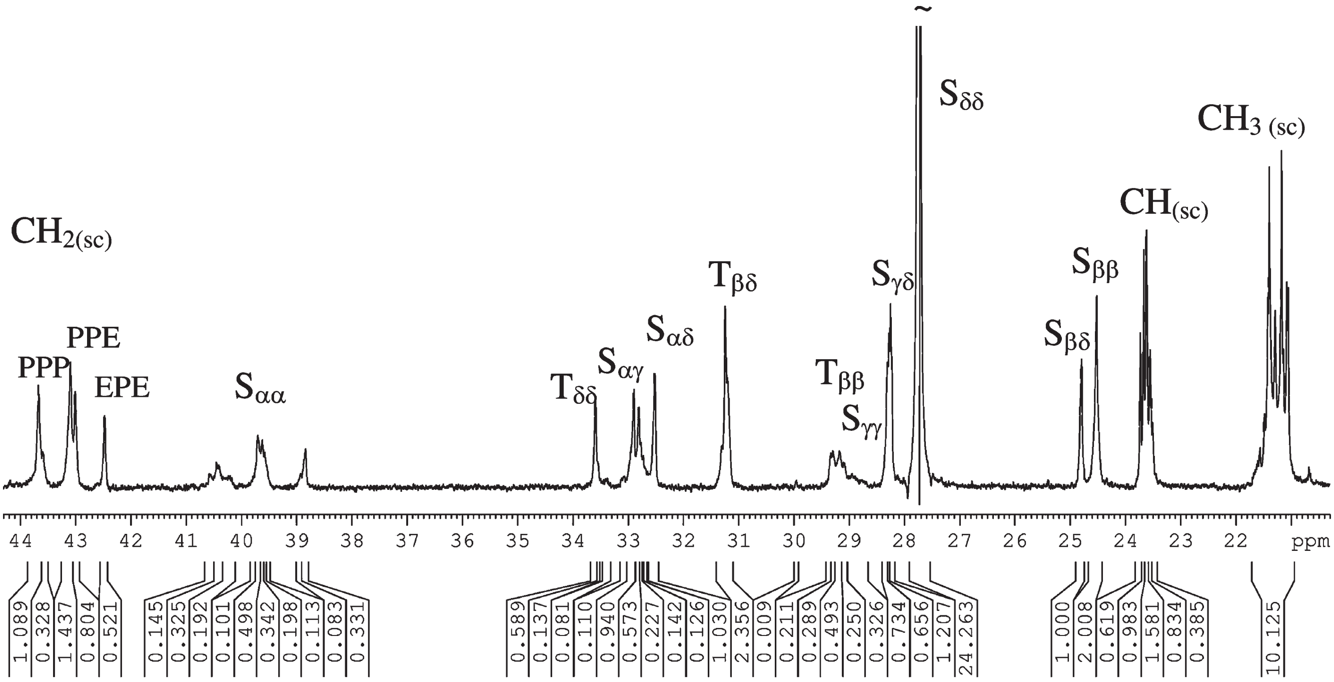


Figure 5. Integrated peaks of ^{13}C NMR spectrum of E/4M1P copolymer with 23.66 mol % (run 6 in Table 1).

Table 2

carbon		chemical shift	area
$S_{\alpha\gamma} + S_{\gamma\delta}$	*1*	28.44−28.17	2.417
$S_{\alpha\delta}$	*2*	32.54	1.030
$S_{\alpha\gamma} + T_{\delta\delta}$	*3*	33.62	0.807
$S_{\alpha\gamma}$	*4*	33.56−32.65	2.118
EPE (CH_2)sc	*5*	42.50	0.521
$S_{\beta\beta}$	*6*	24.54	2.008

According to these assignments, analyzing the HSQC spectrum, all direct $^{1}H-^{13}C$ connectivities were determined and differentiated for comonomer sequences more or less rich in 4M1P. The results can be summarized as follows: (i) $S_{\alpha\alpha(1)}$ resonance, at 38.87 ppm, evidences two protons directly bonded, centered at 1.0718 and 0.9785 ppm; (ii) $S_{\alpha\alpha(2)}$ at 39.66−39.77 ppm, correlates with two directly bonded protons at 1.0377 and 0.9952 ppm, showing a broad resonance; (iii) $S_{\alpha\alpha(3)}$ resonance at 40.43 ppm shows only one correlation peak at 1.0119 ppm, for the related protons.

On the basis of these assignments, all the long-term $^{1}H_{(S\alpha\alpha)}-^{13}C_{(T\beta\beta)}$ correlations were also verified. In detail, $S_{\alpha\alpha(1)}$ and $S_{\alpha\alpha(2)}$ protons correlate through two bonds with the $T_{\beta\beta}$ groups at 29.17 and 29.32 ppm, respectively, which are consequently ascribed to shorter P sequences (EPPE) and longer P sequences (EPPPE□ and PPPPE□).

As previously anticipated, applying this strategy, it became possible to justify and identify more than one signal for the expected $T_{\beta\beta}$ carbon depending on the block length. It is extremely interesting to observe how this effect, related to the block length, becomes evident also for other reported resonances (see for instance Figure 2b in the $CH_{(sc)}$ region; ^{1}H range: 1.5−1.6 ppm).

Comprehensive Check of Consistency of the ^{13}C NMR Assignment. Starting from the whole set of proposed assignments and taking into account the consistency between peak areas and the stoichiometric requirements of the copolymer chain, we set up a procedure[14] for checking the correctness of such assignments starting from the observed integrals of signals of ^{13}C NMR spectra.

Table 3 contains the details of all the proposed assignments. The first column lists the molecular structures that include the carbon being assigned, which is labeled as "$*$". The second column lists the types of carbons. The third column lists the sequences, whose center unit contains the assigned carbon: the carbon under consideration is underlined and symbol □ means P or E. The fourth column lists the chemical shift or the chemical shift range that include all the contributions from the assigned carbon.

The analysis of the spectrum of Figure 5 provides a certain number of peak integrals. For each peak corresponding to one or more signals, we can write a linear equation describing the normalized and observed integral as a function of the unknown molar fractions. We obtain a set of linear equations, whose variables are chosen among the molar fractions. A number of stoichiometric constraints reduce the number of independent variables. Least-squares fitting of the set of equations provides the best solution for the unknown molar fractions. Table 4 presents the observed and calculated values of the normalized peak areas for each distinct and measurable group of signals, along with the sequences types from which the signals arise. For each datum we also report the coefficients of the independent variables considered. The total discrepancy function is given at the bottom of the table. The table shows that the deviations of the error of each equation is not greater than 1.3%.

Although in the spectrum the peaks of $T_{\delta\delta}$, $S_{\alpha\gamma}$, and $S_{\alpha\delta}$ are distinguished, we sum up the contributions in one equation, owing to a partial overlapping of the areas. The integral of CH_3 signals has not been used since it decreases the accuracy of the least-squares fitting.

The present calculation provides a full description of the microstructure of the E/4M1P chain at tetrad level, besides the three PEP-centered pentads. The copolymer tetrad distribution is reported in Table 5. In principle, this information could be used to find the most suitable statistical model of copolymerization.[15]

Table 3. Chemical Shift Assignments for Ethene/4-Methyl-1-pentene Copolymer

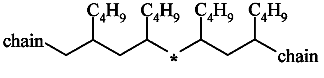
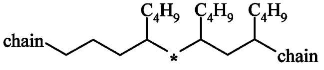
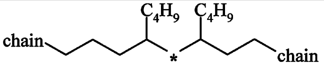
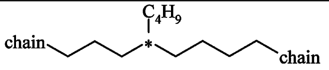
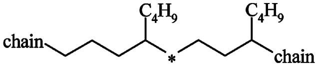
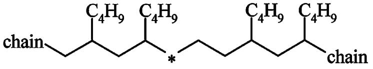
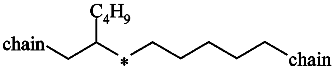
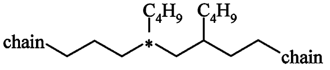
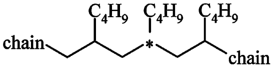
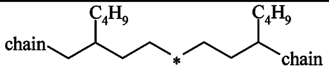
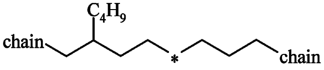
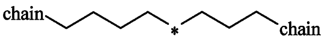
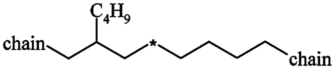
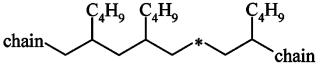
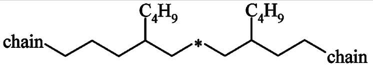
Chemical Structure	Carbon	Sequence	Chemical Shift
CH_2 (sc)	methylene	PP$\underline{\mathrm{P}}$P EP$\underline{\mathrm{P}}$PE PP$\underline{\mathrm{P}}$E EP$\underline{\mathrm{P}}$E E$\underline{\mathrm{P}}$E	43.67 43.60 43.12 43.05 42.50
	S$_{\alpha\alpha}$	PPPPPP PPPPP EPPPPE	40.03 40.43 40.22
		PPPPE EPPPE	39.73 39.66
		EPPE	38.87
	T$_{\delta\delta}$	EEPEE	33.62
	S$_{\alpha\gamma}$	EPEP	33.56 - 32.65
		PPEPP	28.44 - 28.17
	S$_{\alpha\delta}$	PEE	32.54
	T$_{\beta\delta}$	EPP	31.29
	T$_{\beta\beta}$	EPPPE PPPP	29.42 - 29.04
	S$_{\gamma\gamma}$	PEEP	28.65
	S$_{\gamma\delta}$	PEEE	28.23
	S$_{\delta\delta}$	EEEE	27.73
	S$_{\beta\delta}$	PEE	24.81
	S$_{\beta\beta}$	PPEP	24.57
		EPEPE	21.80
CH (sc)	methine	E$\underline{\mathrm{P}}$E EP$\underline{\mathrm{P}}$E PP$\underline{\mathrm{P}}$E PP$\underline{\mathrm{P}}$P EP$\underline{\mathrm{P}}$PE	23.75 23.69 23.64 23.57 23.52
CH_3 (sc)	methyl	EP$\underline{\mathrm{P}}$PE PP$\underline{\mathrm{P}}$P EP$\underline{\mathrm{P}}^{i}$E PP$\underline{\mathrm{P}}^{i}$E E$\underline{\mathrm{P}}$E PP$\underline{\mathrm{P}}^{e}$E EP$\underline{\mathrm{P}}^{e}$E	21.42 21.40 21.40 21.30 21.18 21.08 21.06

Table 4. Least-Squares Fitting of ^{13}C NMR Signals for Sample 6

		normalized peak area			independent variables							
sequence	chemical shift	obsd	calcd	δ (%)	v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8
PPP	43.67−43.60	0.032	0.040	−0.8	1.0	−1.0	1.0	0.0	0.0	0.0	0.0	0.0
PPPE□	43.12	0.051	0.049	0.2	0.0	1.0	−2.0	0.0	−2.0	0.0	0.0	0.0
EPPE□	43.05	0.082	0.076	0.6	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
EPE	42.50	0.064	0.071	−0.7	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
PPPP	40.43−40.03	0.034	0.033	0.1	1.0	−1.5	2.0	0.0	1.0	0.0	0.0	0.0
EPPP	39.73−39.66	0.065	0.076	−1.1	0.0	1.0	−2.0	0.0	−2.0	0.0	0.0	0.0
EPPE	38.87	0.022	0.024	−0.2	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0
EPE + PPEPE + EPEPE + PEE	33.62−32.54	0.204	0.206	0.1	0.0	1.0	1.0	−2.0	0.0	1.0	0.0	1.0
PPE	31.29	0.123	0.125	−0.2	0.0	1.0	−2.0	0.0	0.0	0.0	0.0	0.0
PPP + PEEP	29.42−28.65	0.082	0.079	0.3	1.0	−1.0	1.0	0.0	0.0	0.	1.0	0.0
PEEE + PPEPP	28.44−28.17	0.072	0.071	0.1	0.0	1.0	0.0	0.0	0.0	−1.0	−2.0	−1.0
EEE	27.73	−0.738	−0.738	−0.0	−2.0	−2.5	0.0	3.0	0.0	0.0	1.0	0.0
PEE	24.81	0.052	0.047	0.5	0.0	1.0	0.0	−2.0	0.0	0.0	0.0	0.0
PPEP□	24.57	0.104	0.092	1.3	0.0	0.0	0.0	1.0	0.0	−0.5	0.0	0.5
EPEPE	21.80	0.000	−0.013	−1.3	0.0	0.0	0.0	0.0	0.0	0.5	0.0	−0.5
EPE	23.75	0.074	0.071	0.3	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
EPPE□	23.69	0.075	0.076	−0.1	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
PPPE□	23.64	0.042	0.049	−0.7	0.0	1.0	−2.0	0.0	−2.0	0.0	0.0	0.0
PPP	23.57−23.52	0.030	0.040	−1.0	1.0	−1.0	1.0	0.0	0.0	0.0	0.0	0.0
	R^2 = 0.9987											

$v_1 = f$(P); $v_2 = f$(PE); $v_3 = f$(EPE); $v_4 = f$(PEP); $v_5 = f$(EPPE); $v_6 = f$(PEPE); $v_7 = f$(PEEP); $v_8 = f$(PPEPE)

Table 5. Tetrad Distribution of Ethene/4-Methyl-1-pentene Copolymer with 23.66 mol % Comonomer Content

tetrad	molar fraction
PPPP	0.033
PPPE	0.076
EPPE	0.024
PPEP	0.112
PPEE	0.013
PEPE	0.046
EPEE	0.034
PEEP	0.008
PEEE	0.031
EEEE	0.623

Conclusions

The present work represents a successful completion of the previous attempts to assign the ^{13}C NMR spectra of E/4M1P copolymers. The basis of our investigation was the attainment of a wide range of chemical composition of the copolymers, expanding the 4M1P molar content up to 90%, by using the catalytic system *rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl$_2$/methylaluminoxane.

First, the newly collected data allowed us to solve the ambiguous assignment of a few methylene carbons of the main chain, namely methylenes $S_{\gamma\delta}$ and $S_{\alpha\gamma}$. The results presented show the utility of the quantitative self-consistency check as a tool to refine NMR peaks assignment. Furthermore, we were able to identify and justify more than one signal for the $T_{\beta\beta}$ carbons, depending on the block length and comonomer sequences. This improvement was obtained by analyzing the previous data in the light of the new systematic self-consistent approach and by exploiting fundamental 2D gradient-assisted techniques.

On the basis of the achieved assignment, the microstructural analysis by ^{13}C NMR of such copolymers was completely obtained at tetrad level by a methodology that exploits all the peak areas of the spectra and accounts for the stoichoimetric requirements of the copolymer chain. The quantitative determination of the microstructure of these copolymers will allow us to progress in clarifying the polymerization mechanism.

Experimental Section

General Remarks. Manipulations of air- and/or moisture-sensitive materials were carried out under an 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 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. Nitrogen and ethene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4 Å molecular sieves.

Copolymerization. The copolymerizations were typically performed at 45 °C in a 300 mL glass reactor equipped with a magnetic stirrer and an inlet tube for the bubbling of the gaseous comonomer. The reactor was filled with 100 mL of anhydrous toluene, 4M1P in the proper ratio, and MAO in toluene (6 mmol of MAO). After thermal equilibration of the reactor system, ethene was continuously added until saturation. The polymerization was typically started by adding a solution containing 2 μmol of the metallocene. The pressure of ethene was kept constant at 1.03 bar for all the experiments. The copolymerization was terminated by adding small amounts of ethanol and of dilute hydrochloric acid, and polymers were precipitated by pouring the whole reaction mixture into an ethanol excess (1.5 L), to which a proper amount of concentrated hydrochloric acid had been previously added. The copolymer was collected by filtration and dried under vacuum at 70 °C.

Nuclear Magnetic Resonance (NMR). Samples were dissolved in $CDCl_2CDCl_2$ (TCE) to acquire the NMR experiments; hexamethyldisiloxane was used as internal chemical shift reference. All the spectra were acquired on a Bruker AVANCE-400 spectrometer operating at 100.58 MHz and at 103 °C. ^{13}C conditions: 10 mm probe; 14.30 μs as 90° pulse; 32K data points, acquisition time 2.14 s, relaxation delay 18 s, 3K transients. Proton broadband decoupling was achieved using bi_walz16_32 power-gated decoupling.

Gradient-assisted 2D HSQC and HMBC spectra were acquired on the same spectrometer with a 5 mm PFG probe, operating at 103 °C.

Two dimension NMR parameters: 90° pulse widths for ^{1}H and ^{13}C were 9.05 and 14.00 μs, respectively; relaxation delay 3.0 s.

g-HSQC experiments were carried out with a delay of 1.92 ms (corresponding to a $^1J_{CH}$ = 130 Hz) for creation of antiphase magnetization;. 1.2 kHz as spectral width in the ^{1}H dimension and 6.04 kHz in the ^{13}C dimension; coherence selection for PFG pulse was 2.0 ms long. Data were zero-filled and weighted with a shifted sinebell function before Fourier transformation.

g-HMBC experiments, with 2-fold low-pass J-filter, were carried out with a delay of 125 ms for the evolution of long-range coupling and delays corresponding to $^1J_{CH}$'s of 120 and 140 Hz for the creation of the antiphase magnetization. Spectral width was 1.2 kHz in the ^{1}H dimension and 6.04 kHz in the ^{13}C dimension. Data were zero-filled and weighted with a shifted sinebell function before Fourier transformation.

Molecular Analysis. The molecular weight averages and the molecular weight distribution (MWD) were obtained by a high-temperature GPCV 2000 system (from Waters) equipped with two online detectors, a differential viscometer, and a refractometer. GPC separation was performed adopting the following experimental conditions: three PL Gel Olexis columns from PL, *o*-dichlorobenzene as the mobile phase, 0.8 mL/min of flow rate, and 145 °C of temperature. For GPC calibration, polystyrene standards with molar masses ranging from 162 to 3.3 10^6 g/mol were used.

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