

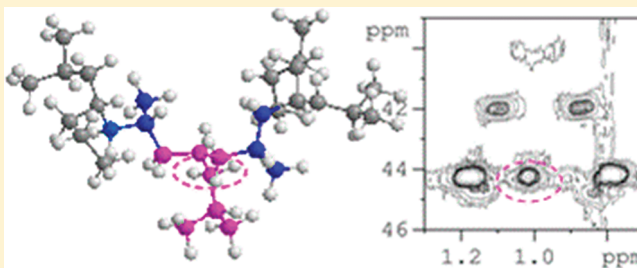
# Propene/4-Methyl-1-pentene Copolymers by Metallocene-Based Catalysts: First Insight into $^{13}\text{C}$ NMR Assignment

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Supporting Information

**ABSTRACT:** A thorough  $^{13}\text{C}$  NMR analysis of a series of propene/4-methyl-1-pentene copolymers, prepared with the isoselective metallocene precatalyst [*rac*-(EBTHI)ZrCl<sub>2</sub>], has paved the way to the first full description of such potentially interesting family of copolymers at the triad level. Several tetrads and even longer sequences were assigned and quantified as well. The main problem, consisting in the partial overlap of the resonances of the  $\alpha\alpha$ -methylenes of the chain and the  $\alpha$ -methylenes of the branch, generally utilized for the microstructural description of propene/linear higher  $\alpha$ -olefins copolymers, was overcome by analyzing other less informative regions of the spectra along with the application of two-dimensional heteronuclear ( $^1\text{H}$ – $^{13}\text{C}$ ) correlation measurements. A computational procedure for checking the correctness of the proposed assignments was applied to the  $^{13}\text{C}$  NMR observed integrals of two samples differing in comonomer compositions. In both cases, a correspondence between the observed and calculated values of the sequence molar fractions was found.



## INTRODUCTION

Since the discovery by Kaminsky, Sinn, and Ewen of the methylaluminoxane (MAO)-activated metallocene-catalyzed polymerization with high activity and stereoselectivity, several reports have been published dealing with propene copolymerization with linear  $\alpha$ -olefins (e.g., 1-butene, 1-hexene, and 1-octene).<sup>1</sup> In more recent years, and as a consequence of the discovery of novel metallocene and post-metallocene complexes capable of incorporating bulky comonomers at unprecedented amounts, new attention was centered in  $\alpha$ -olefin copolymerization with sterically hindered comonomers.

A promising family of sterically hindered monomers is represented by branched  $\alpha$ -olefins, like 4-methyl-1-pentene (4M1P),<sup>2</sup> which is the object of the present study. The synthesis of copolymers with variable content of 4-methyl-1-pentene, which offers a larger specific volume due to its branching, is expected to be a feasible route for tuning the diffusion properties of materials for gas separating applications (e.g., membranes and hollow fibers) and/or for permeable films destined to particular packaging requirements.

There are several, mostly recent, publications on ethene-based copolymers with 4M1P. A noticeable contribution to the understanding of the microstructural features of such copolymers was offered by some of us and consisted in the complete peak assignment of the  $^{13}\text{C}$  NMR spectra of variously microstructured ethene/4M1P copolymers.<sup>3</sup> Thanks to our work, the correct evaluation of ethene/4M1P copolymer microstructure at triad and tetrad level in the entire range of comonomer composition (comprehensive of the calculation of the amount of possible regioirregular sequences) is now available. The copolymerization

parameters of however microstructured samples of this family of copolymers can be now correctly evaluated.

Taking into account that random propene-based copolymers are the most widely used materials for packaging, the chance of modulating polypropene features, through the control of content and distribution of the branching, appears of high interest to obtain target values of thermal and mechanical properties as well as of polymer density and free volume. Rather surprisingly, only a few publications dealing with propene (P)-based copolymers of 4M1P by metallocene catalysts are to be found in the literature. Most of them aimed at investigating the influence of the branched side chain on the final properties of the copolymers compared to those observed with conventional linear comonomers (e.g., 1-hexene, 1-octene, 1-decene).<sup>4</sup> Moreover, at the best of our knowledge, the  $^{13}\text{C}$  NMR assignment of the spectra of P/4M1P copolymers still relies on a couple of works. In the former one, by some of us, only two samples, both at very low 4M1P content, obtained from two different isoselective metallocene catalysts were studied.<sup>1d</sup> Some analysis of P/4M1P copolymers, containing up to 18 mol % 4M1P, obtained with novel sterically expanded derivatives of the classical syndiospecific metallocene catalyst, was recently presented.<sup>5</sup>

The main objective of the present work here presented was to extend and deepen the microstructural characterization of P/4M1P copolymers by  $^{13}\text{C}$  NMR by (i) checking chemical shifts previously assigned and (ii) accomplishing all possible new

Received: December 22, 2010

Revised: February 24, 2011

Published: April 07, 2011

**Table 1.** Propene/4-Methyl-1-pentene Copolymerization from *rac*-(EBTHI)ZrCl<sub>2</sub> and MAO as the Catalytic System<sup>a</sup>

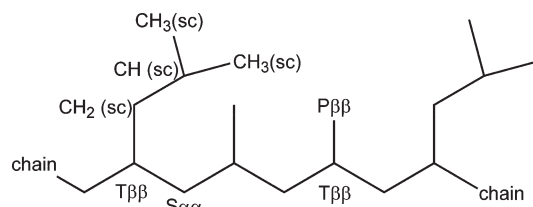
run	$f^b$ (mol/mol)	yield (mg)	$t_{pol}$ (min)	activity $\times 10^{-3}$ (mg <sub>pol</sub> /(mmol <sub>Zr</sub> h bar))	Y% <sup>c</sup> (mol)	$M_w^d$	$M_w/M_n^d$	monomer conversion (%)
1		450	30	238	0	12000	1.8	
2	0.10	472	10	2406	1.88	20500	2.1	2.9
3	0.20	460	10	2345	3.57	16400	1.9	2.5
4	0.30	1020	10	2213	5.70	9700	1.8	5.8
5	0.54	235	10	503	9.92	10800	1.8	1.3
6	0.82	1220	15	754	15.74	6700	1.8	5.8
7	1.03	1330	15	1202	18.72	7900	1.8	5.9
8	2.12	1102	15	1166	35.88	n.d. <sup>e</sup>	n.d. <sup>e</sup>	3.6
9	3.00	628	30	388	43.00	6800	1.8	2.0
10	4.00	1548	45	562	53.27	7400	1.8	4.2
11	4.75	390	45	146	60.75	6100	1.9	1.1
12	6.00	1428	90	136	67.21	n.d. <sup>e</sup>	n.d. <sup>e</sup>	2.9
13	0	4475	30	447	100	n.d. <sup>e</sup>	n.d. <sup>e</sup>	-

<sup>a</sup> Polymerization conditions: total volume = 100 mL, [catalyst] = 1.1 at 10  $\mu$ mol, Al/Zr = 3000 (mol/mol),  $T = 30$  °C,  $P = 1.08$  atm. <sup>b</sup> 4M1P/P feed ratio (mol/mol) in liquid phase. <sup>c</sup> From <sup>13</sup>C NMR analysis. <sup>d</sup> Molecular weight from GPC analysis. <sup>e</sup> n.d. = not determined.

sequence assignments, by means of the analysis of a set of copolymers *ad hoc* synthesized in a wide compositional range. As a catalyst, the prototypical hydrogenated metallocene, *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride [*rac*-(EBTHI)ZrCl<sub>2</sub>] (EBTHI), free of substituents on the indenyl ligand, was used. This catalyst is not suitable for industrial applications because of the low molecular weights of the produced copolymers. However, it is sufficiently iso- and regioselective to allow for the preparation of copolymers in which the spectral multiplicity can mainly be ascribed to differences in comonomer sequences. Moreover and more interestingly, it promotes an easy incorporation of bulky comonomers, thus allowing for the production of acceptable yields of copolymers over the entire range of comonomer composition.

For the <sup>13</sup>C NMR assignments of P/4M1P copolymers, the obvious comparison with the previously reported assignments of the copolymers of propene and linear higher  $\alpha$ -olefins is poorly helpful.<sup>1c,d</sup> Indeed, the  $\alpha\alpha$ -methylenes, which are generally utilized for an easy and unambiguous description of propene/linear higher  $\alpha$ -olefins copolymers at the tetrad level, and the  $\alpha$ -methylenes of the branch, which could potentially allow for the identification of the 4M1P centered triads and pentads, here fall in the same spectral region. Thus, in order to fully describe these copolymers at the triad and/or tetrad level, our investigations had to take into consideration other spectral regions, generally considered less informative, and were based on several points: (i) comparison of the <sup>13</sup>C NMR spectra of P/4M1P copolymers in a wide range of compositions, (ii) comparison with the <sup>13</sup>C NMR spectral patterns of ethene/4M1P copolymers obtained with the same catalyst, (iii) correlation between integrated peak areas of signals of sequences linked by stoichiometric relationships, and (iv) application of two-dimensional NMR techniques, including homonuclear <sup>1</sup>H–<sup>1</sup>H and heteronuclear <sup>1</sup>H–<sup>13</sup>C experiments, on selected samples.<sup>6,7</sup> This last procedure was of great help in distinguishing the signals of the different kinds of methylenes in the  $\alpha\alpha$ -methylene region.

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

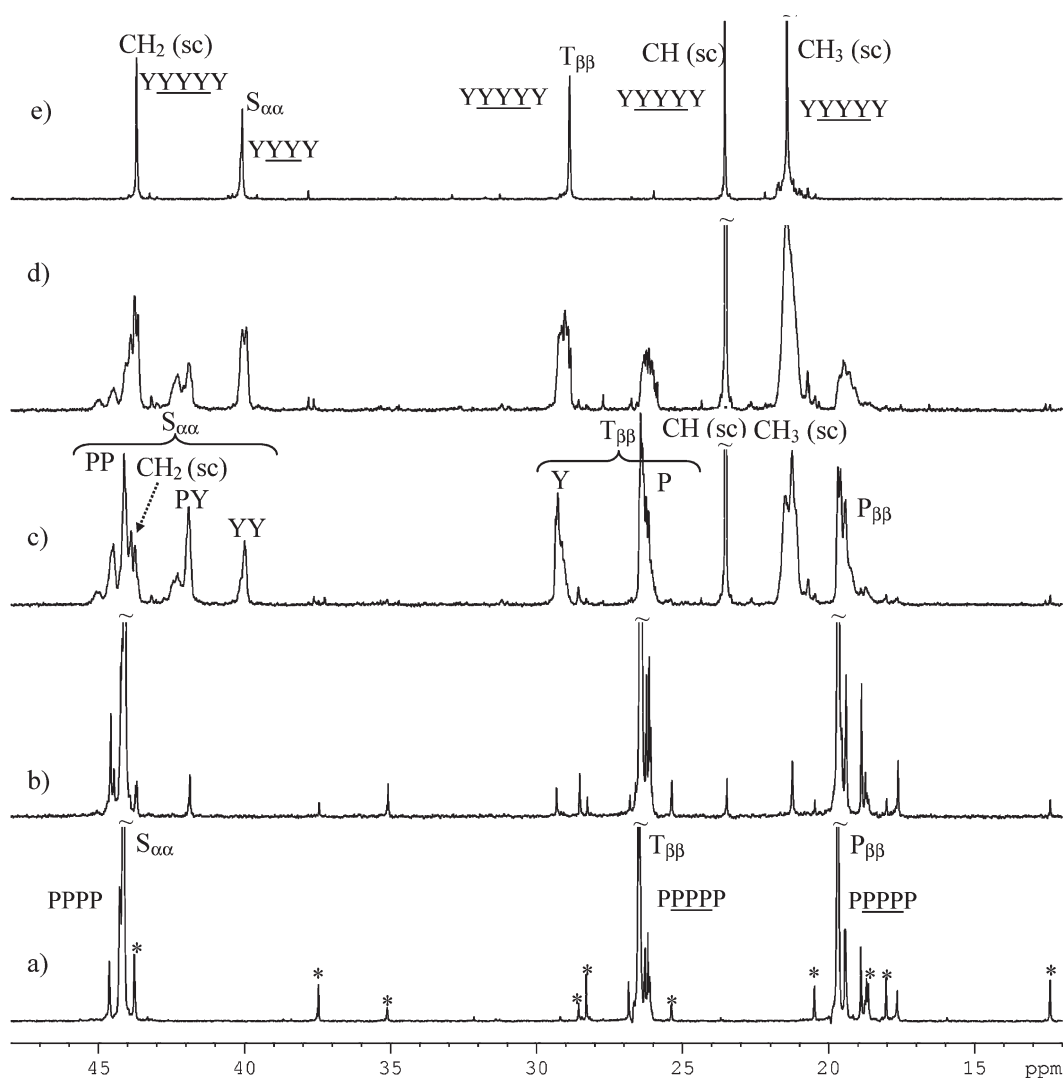
**Scheme 1.** Structure and Carbon Numbering of P/4M1P Copolymer

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Copolymers.** A series of P/4M1P copolymerizations were conducted with the EBTHI-MAO catalyst at the [Al]/[Zr] molar ratio of 3000 in toluene at 30 °C. A range of [4M1P]/[P] feed ratios from 0.1 to 6.0 mol/mol was investigated, allowing for the preparation of copolymers with a 4M1P content from about 2 to 65 mol %. In Table 1 the data collected for P/4M1P copolymers are reported along with the polymerization conditions. We refrain from commenting on the trends of the activities since our aim was mainly to obtain copolymer samples with homogeneous comonomer composition suitable for microstructural investigation. In particular, to maintain nearly constant the comonomer concentration in solution throughout the whole course of the reaction, the conversion of both comonomers was kept lower than 6%, following an experimental approach already reported by some of us.<sup>8</sup> It is worth underlining that the use of a good solvent as toluene, the low monomer conversion, and the consequent low polymer concentration in the polymerization medium allowed us to assume that a homogeneous polymerization solution was obtained and that the comonomer concentration on the catalytic center was reasonably constant. In this paper, “P” and “Y” are used to indicate propene and 4-methyl-1-pentene monomer units, respectively, in the descriptions of monomer sequence distributions.

The general structure and carbon numbering of an isotactic P/4M1P copolymer chain are sketched in Scheme 1.

The carbons were labeled according to the nomenclature first defined by Carman<sup>9</sup> and modified by Dorman<sup>10</sup> and Randall,<sup>11</sup>



**Figure 1.**  $^{13}\text{C}$  NMR spectra of P/4M1P copolymers with different comonomer content: (b) 1.88 mol % (run 2 in Table 1), (c) 35.88 mol % (run 8 in Table 1), and (d) 60.75 mol % (run 11 in Table 1). The spectra of the P (a) and 4M1P (e) homopolymers are reported as points of reference. Chain-end groups and regioirregularities are starred in spectrum a.

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 were identified by a pair of Greek letters to indicate the distance to branches in either directions. Methyl, methylene, and methine carbons in the side chain were designated by the symbols  $\text{CH}_3(\text{sc})$ ,  $\text{CH}_2(\text{sc})$ , and  $\text{CH}(\text{sc})$ .

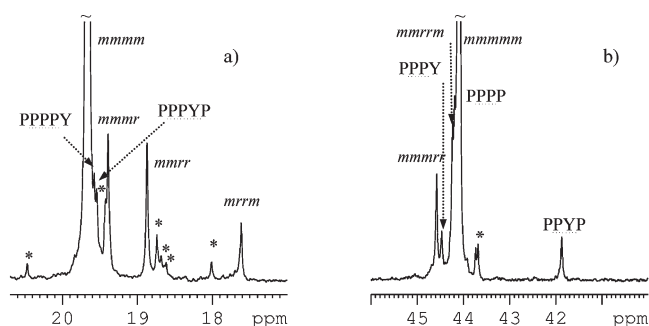
Figure 1 shows the  $^{13}\text{C}$  NMR spectra of a selected series of P/4M1P copolymers at increasing comonomer content along with those of the two homopolymers, taken as references. Because of the low molecular weights produced by catalyst EBTHI, there are several signals (from now on starred in the spectra along with the resonances attributed to the regioirregularities) belonging to a variety of chain-end groups. In the spectrum of polypropylene (Figure 1a), besides the main peaks of methyl, methine, and methylene carbons, the quite intense signals of saturated *n*-propyl (12.42, 18.02, 18.70, 28.28, and 37.46 ppm) and unsaturated vinylidene (20.53 ppm) chain-end groups are indicated, along with the signals due to 1,3 enchainments (18.76, 25.39, 28.58, and 35.16 ppm).<sup>12–14</sup>

The comparison with the spectra of the homopolymers (Figure 1a,e) allowed for the easy assignment of the P and Y

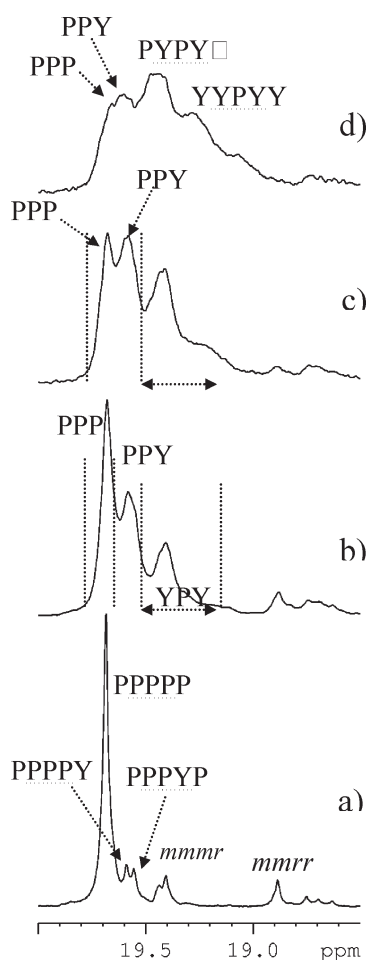
homotetrads and pentads in the copolymers. The analysis of the spectrum in Figure 1b, at low comonomer content (1.88 mol %), allowed us to check the previous assignments of the sequences containing isolated Y units.

Indeed, in Figure 2, where the expanded spectral regions of the propene methyl and  $\alpha\alpha$ -methylene carbons of Figure 1b are shown, beside the signals due to irregular stereosequences and chain-end groups (starred in the spectra), further resonances are well detectable, even if only a few are quantitatively measurable. In the methyl region it was easy to assign the pentads richest in propene:  $\text{PPPPY}$  and  $\text{PPYPY}$  at 19.59 and 19.55 ppm, of similar intensities.<sup>15</sup> Likewise, in the  $\alpha\alpha$ -methylene region (Figure 2b) it was possible to confirm the previous assignment of PP and PY centered tetrads richest in propene at 44.48 ppm ( $\text{PPPY}$ ) and 41.90 ppm ( $\text{PPYP}$ ), respectively.

By inspection of the spectra of Figure 1c,d, one could easily observe that the copolymers with increasing 4M1P content present a noticeably higher level of complexity. In several cases, not only the quantitative evaluation but also the mere identification of the sequences was quite complicated due to the merging of signals



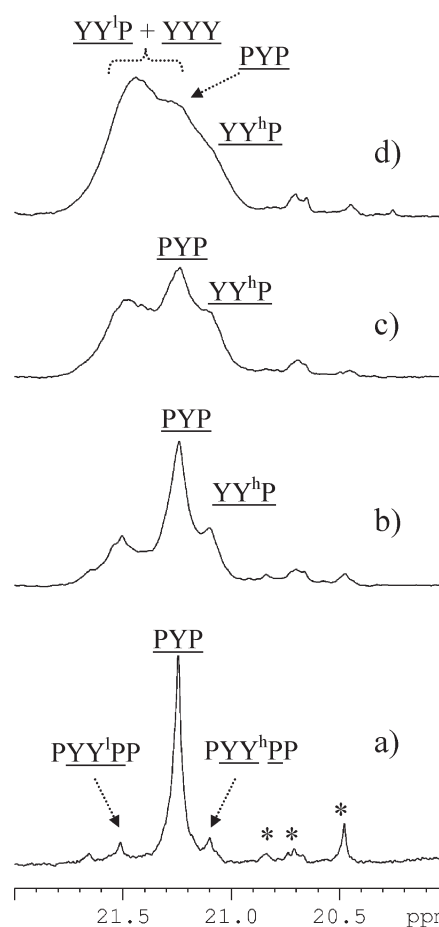
**Figure 2.** Methyl (a) and methylene (b) region of the spectrum of P/Y copolymer with 1.88 4M1P molar content (run 2 in Table 1). Chain-end groups and regioirregularities are starred.



**Figure 3.** Expanded plot of the region of the propene methyl at increasing comonomer content: (a) 5.70 mol % (run 4 in Table 1); (b) 18.72 mol % (run 7 in Table 1); (c) 35.88 mol % (run 8 in Table 1); (d) 67.21 mol % (run 12 in Table 1).

belonging to different structures. For the sake of clarity, in the following, we will analyze and discuss separately the different spectral regions, at the same time distinguishing between the peaks identified and those quantitatively measurable.

**Methyl Region (from 17 to 22 ppm).** Figure 3 presents the expanded spectral region of the propene methyls at increasing comonomer content.

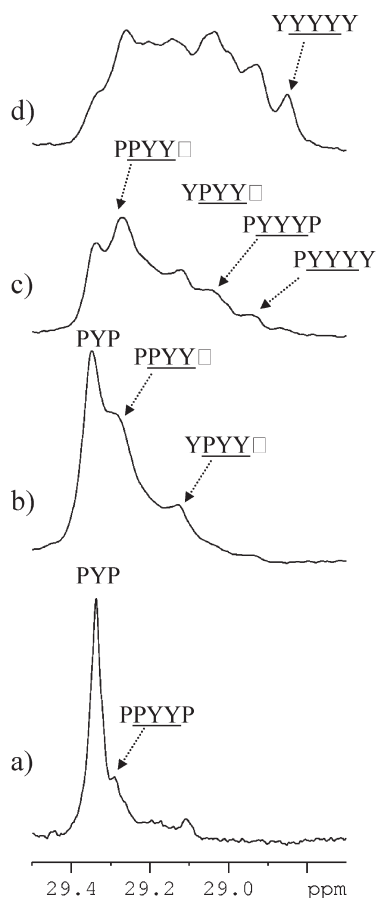


**Figure 4.** Expanded plot of the spectral region of side chain methyl carbons of P/4M1P copolymers of four different compositions: (a) 5.70 mol % (run 4 in Table 1); (b) 18.72 mol % (run 7 in Table 1); (c) 35.88 mol % (run 8 in Table 1); (d) 53.27 mol % (run 10 in Table 1). Chain-end groups and regioirregularities are starred.

In the copolymer containing 5.7 mol % of comonomer (Figure 3a), we still easily detected the already assigned signals of the sequences richest in P units: PPPPP, PPPPY, and PPPYP in the region from 19.82 to 19.50 ppm. In the spectra of the copolymers with higher comonomer content (Figure 3b–d) the three PPY-centered pentads richer in Y units (PPPYY, YPPYY, YPPYP), besides the overlap with the irregular mmmr stereosequence (at 19.40 ppm), are poorly resolved and cannot but be assigned to the region from 19.43 to 19.40 ppm. It is possible to identify the region of the YPY-centered pentads (in analogy with the assignment of all the other copolymers of propene with linear higher  $\alpha$ -olefins<sup>1c,d</sup>) from 19.33 to 19.11 ppm. Within this region, two of the three possible signals of the YPY-centered pentads, YPPYY, PYPYY, and PYPYP, are well detectable. On the basis of the growing trend of the peak intensities, we have assigned the more intense signal at 19.31 ppm to the unresolved pair PYPYP and PYPYY (PYPY□) and that at 19.11 ppm to the YPPYY pentad. From now on, the symbol □ means Y or P in all pairs of sequences which are indistinguishable.

Figure 4 shows the expanded plot of the spectral region of the side chain methyl carbons for four different compositions (5.70, 18.72, 35.88, and 54.12 mol %, respectively).

Taking the signal of the PYP sequence (easily assigned at 21.24 ppm in the spectrum of Figure 4a of the copolymer with the

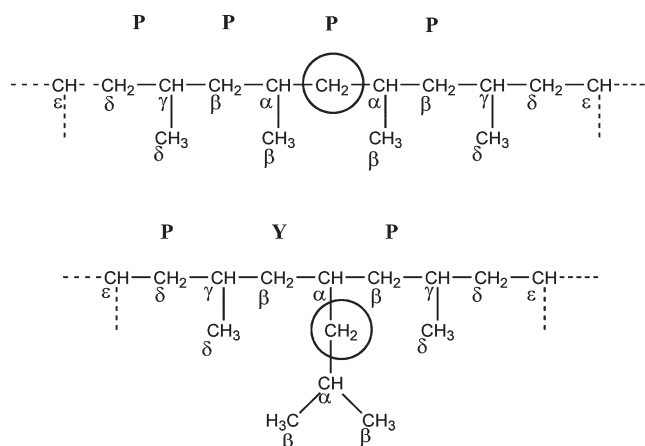


**Figure 5.** Expanded plot of the spectral region of methine carbons of backbone for four different compositions: (a) 5.70 mol % (run 4 in Table 1); (b) 18.72 mol % (run 7 in Table 1); (c) 35.88 mol % (run 8 in Table 1); (d) 53.27 mol % (run 10 in Table 1).

lowest comonomer content) as a reference, we observed the presence of two small resonances of similar intensities at higher (21.10 ppm) and lower (21.51 ppm) field. Taking into account the assignments of the corresponding sequences performed in ethene/4-methyl-1-pentene copolymers,<sup>3</sup> we assigned the resonance at higher field to the more shielded methyl carbon of the  $\text{PYYPP}$  sequence and consequently the one at lower field to the less shielded methyl carbon of the same  $\text{Y}$  unit. From now on, we will conventionally denote the two different methyls as  $\text{Y}^{\text{h}}$  (high field) and  $\text{Y}^{\text{l}}$  (low field). A reasonable explanation of such a signal splitting is the following. While in the  $\text{PYP}$  sequence the two side-chain methyl groups are magnetically equivalent, and in particular they have the same probability of being in the  $\gamma$ -gauche conformation with respect to the main-chain  $\text{CH}$ , in the sequence  $\text{PYYPP}$  the different steric hindrance of the side chains of the adjacent  $\text{Y}$  and  $\text{P}$  units produces an unbalance in the probability of the  $\gamma$ -gauche interaction with  $\text{CH}$  of the two diastereotopic methyl groups of the central  $\text{Y}$  unit. Hence, their signals shift to higher or lower field depending on their meso/racemic relationship with the  $\text{Y}$  and  $\text{P}$  substituents of the chiral  $\text{CH}$ .<sup>16</sup>

At increasing comonomer content, we can observe that these two signals, which in Figure 4a have the same intensity, appear unbalanced (Figure 4b–d), the signal at lower field appearing more and more intense than the other one and tending to merge with the signal assigned to the  $\text{YYYYY}$  pentad in the spectrum of

**Scheme 2.** Sketched Spectral Equivalence of the  $\alpha\alpha$ -Methylenes of the Chain and the  $\alpha$ -Methylenes of the Branch



4M1P homopolymer (21.40 ppm). This is an evidence of the correct assignment of the  $\text{PYY}^{\text{h}}\text{PP}$  pentad.

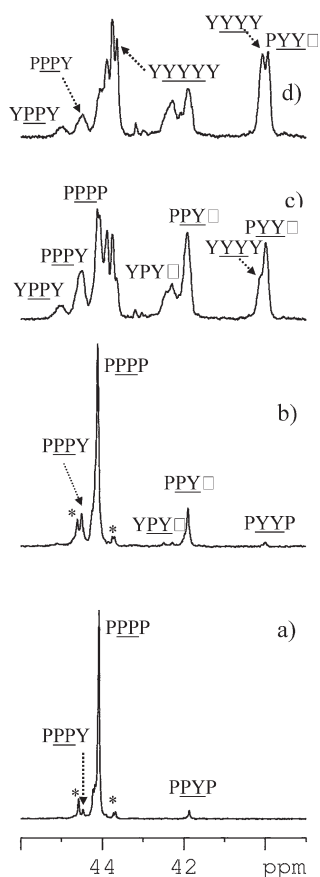
Also, the upfield  $\text{YY}^{\text{h}}\text{P}$ -centered pentads cannot be distinguished, since, at increasing comonomer content, only a broadening of the signal at 21.10 ppm assigned to the  $\text{PYY}^{\text{h}}\text{PP}$  pentad is observed.

**Methine Region (from 23 to 30 ppm).** The analysis of the methine region of propene as well as of that of the  $\text{CH}(\text{sc})$  did not supply further information with respect to the above better resolved methyl region.

We have carefully analyzed the backbone methine carbon of 4M1P, which is richer in information. Figure 5 shows the expanded plot of the spectral region of such a methine for four different compositions (5.70, 18.72, 35.88, and 53.27 mol %, respectively).

The main resonance, appearing at 29.34 ppm in the spectrum of the copolymer at the lowest comonomer content (Figure 5a), was assigned to carbon  $\text{T}_{\beta\beta}$  of the isolated  $\text{Y}$  in the  $\text{PYP}$  triad. In Figure 5a, the resonance poorly resolved from the main signal at 29.29 ppm was assigned to the  $\text{PPYY}^{\text{h}}\text{P}$  pentad by comparison with the intensity of the corresponding well-resolved signals of methyls  $\text{Y}^{\text{h}}$  and  $\text{Y}^{\text{l}}$  of Figure 4a. At increasing 4M1P content such a signal becomes indistinguishable from that of the  $\text{PPYY}^{\text{h}}\text{P}$  pentad. In Figure 5b, the minor signal at 29.11 ppm cannot but be assigned to the pairs of pentads  $\text{YPYY}^{\text{h}}\text{P}$  and  $\text{YPYY}^{\text{l}}\text{P}$ . At increasing 4M1P concentration, three other resonances appear. The resonance at 28.85 ppm was assigned to the  $\text{YYYYY}$  pentad by comparison with the spectrum of 4M1P homopolymer. By observing the variation trend among the peak intensities with increasing comonomer content (Figure 5c,d), we reasonably assigned the resonances at 29.03 and 28.93 ppm to the two  $\text{YYY}$  centered pentads, namely  $\text{PYYYYP}$  and  $\text{PYYYYY}$ , respectively.

**Methylene Region (from 39 to 46 ppm).** As already mentioned, the assignment of the methylene region was quite problematic since the most informative resonances, namely, those of the  $\alpha\alpha$ -methylenes of the  $\text{PP}$ -centered tetrads and of the  $\alpha$ -methylenes ( $\text{sc}$ ) of the  $\text{Y}$ -centered pentads, fall in the same region and are partially overlapped. Such a phenomenon is easily accounted for by the Grant and Paul additivity rules<sup>17,18</sup> that predict exactly the same location for the  $\alpha\alpha$ -methylene of the  $\text{PPPP}$  tetrad and for the  $\alpha$ -methylene of the branch in the  $\text{PYP}$  sequence. Such a predicted spectral equivalence is sketched in Scheme 2.

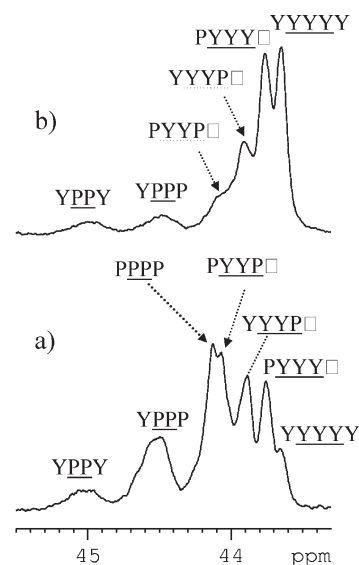


**Figure 6.** Expanded plot of methylene region for P/4M1P copolymer at increasing comonomer content: (a) 1.88 mol % (run 2 in Table 1); (b) 9.92 mol % (run 5 in Table 1); (c) 43.00 mol % (run 9 in Table 1); (d) 60.75 mol % (run 11 in Table 1). Stereoirregular sequences are starred.

The overlap of the two kinds of methylenes did not prevent the assignment of several PP-, PY-, and YY-centered sequences, which was mainly performed by following the growing trend of the signals of copolymers in a wide range of compositions, but made their quantitative evaluation quite complicated. In the following, we will discuss separately the assignment of the  $\alpha\alpha$ -methylenes of the chain and that of  $\alpha$ -methylenes of the branch.

**Chain  $\alpha\alpha$ -Methylenes.** Figure 6 shows the expanded plot of the spectral methylene region for the four following compositions: 1.88, 9.92, 43.00, and 60.75 mol %. The PPPP tetrad was easily assigned from the spectrum of propene homopolymer at 44.10 ppm. At all copolymer compositions of Figure 6, the signal at 44.48 ppm, previously assigned to the PPPY sequence in the sample richest in propene of Figure 2b, is well detected. The downfield resonance appearing in the spectra of Figure 6c,d at about 45 ppm cannot but be assigned to the YPPY tetrad. Both PPPY and YPPY tetrads are almost quantitatively measurable at all the copolymer compositions.

The assignment of the PY and YY  $\alpha\alpha$ -methylenes was performed in analogy with that of all the other propene/linear  $\alpha$ -olefin copolymers.<sup>19</sup> In the spectrum of Figure 6a, corresponding to the lowest 4M1P content, the already assigned tetrad PPYP is clearly visible. At increasing 4M1P concentration the four PY-centered tetrads are only partially resolved (YPPY is indistinguishable from YPPY and the same is true for the pair PPYP and PYY). The resonances of the two pairs YPY□ and PYY□ were assigned at 42.28 and 41.90 ppm, respectively.



**Figure 7.** Expanded plot of methylene region for P/4M1P copolymer at high comonomer content: (a) 43.00 mol % (run 9 in Table 1) and (b) 67.21 mol % (run 12 in Table 1).

In Figure 6b, a single signal is detected for the YY-centered tetrads at 39.90 ppm. The analysis of the spectra of copolymers of Figure 6c,d gave us the chance of identifying the YYYYP tetrad at 40.05 ppm, corresponding to the resonance of the homopolymer, the upfield signal belonging to PYY□ tetrad at 39.90 ppm. All the above assigned tetrads and/or pairs of tetrads are quantitatively measurable at almost all the copolymer compositions.

**Branch  $\alpha$ -Methylenes.** The branch  $\alpha$ -methylenes of the YYY- and PYY-centered pentads can be assigned on the spectra of two copolymers richer in 4M1P (43.00 and 67.21 mol %, respectively), whose expanded regions from 43 to 46 ppm are shown in Figure 7. By comparison with the spectrum of the homopolymer, we assigned the YYYYP pentad at 43.65 ppm. The three pairs of pentads PYY□, YYYYP□, and PYYYP□ were assigned on the basis of the reciprocal intensity variation at increasing comonomer content. The assignment of the PYP triad was performed by 2D NMR experiments conducted on selected samples and is described in the following section.

**Two-Dimensional NMR Techniques.** In order to discriminate and unambiguously assign a few resonances related to the comonomer sequences, a selection of copolymers at different comonomer contents was extensively investigated by acquiring heteronuclear  $^1\text{H}$ - $^{13}\text{C}$  experiments based on one-bond correlations (HSQC) and long-range correlations (HMBC). Check and extension of previously assigned signals have been possible.

The analysis of the first sample endowed with a low comonomer content (3.57 mol %) evidenced a good agreement between the assignments made on the basis of previously collected 1D experiments but did not exhibit more peaks. On the contrary, the HSQC spectrum (Figure 8a) of a sample richer in the Y unit (15.74 mol %) showed a cross-peak at  $\delta_{\text{C}} = 44.20$  ppm and  $\delta_{\text{H}} = 1$  ppm, placed at the same  $^{13}\text{C}$  chemical shift of the  $S_{\alpha\alpha}$  methylene PP-centered signal.

The corresponding HMBC spectrum (Figure 8b) allowed to assign this signal to the branch  $\alpha$ -methylene of a PYP sequence. In fact, the  $\text{CH}_2$  protons at about 1 ppm exhibited a three-bond correlation with their own  $\text{CH}_{3(\text{sc})}$  carbons at 21.24 ppm and two two-bond correlations with their own  $\text{T}_{\beta\beta}$  carbon at 29.43 ppm and

$\text{CH}_{(\text{sc})}$  carbon at 23.50 ppm. In addition, and most important, the  $\text{CH}_2$  protons exhibit only one three-bond correlation with a  $\alpha\alpha\text{-CH}_2$  of a P unit at about 42 ppm, suggesting that they belong to a symmetric PYP sequence (Scheme 3). In case of a PYY sequence were present, we would expect a three-bond cross correlations of these protons with the YY  $\alpha\alpha\text{-CH}_2$  carbons at 39.90 ppm, which actually is not detected.

**Comprehensive Consistency Check of the Proposed Assignments.** Table 2 contains all the details of the proposed assignments. The first column lists the molecular structure that includes the carbon being assigned, labeled as “\*”. The second column lists the kind of assigned carbon. The third column reports the sequences whose center unit contains the assigned carbon. The fourth and fifth columns list the corresponding compositional or steric sequences. In the last column, the chemical shifts are reported.

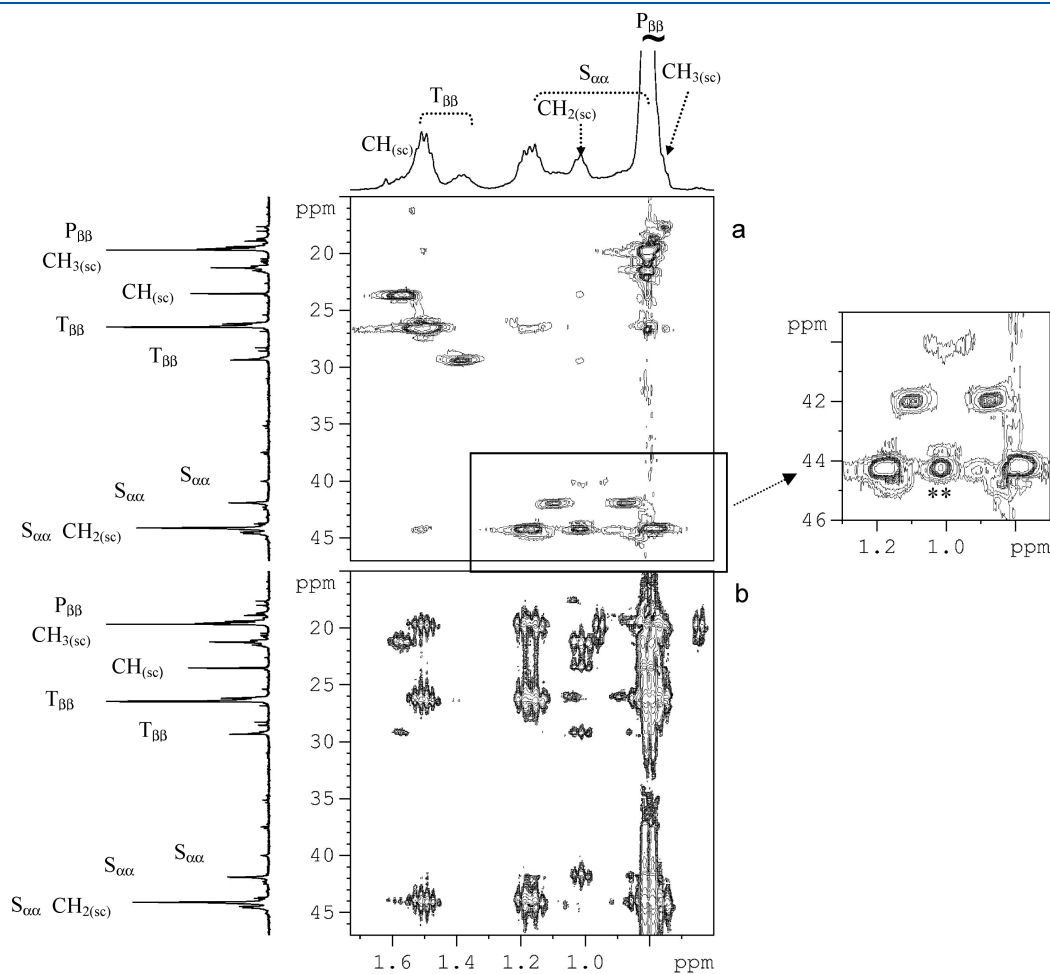
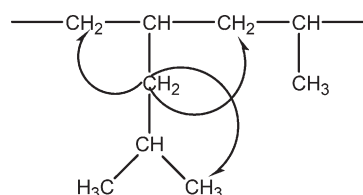
Starting from the whole set of proposed assignments and taking into account the consistency between peak areas and the stoichiometric requirements of the copolymer chain, we applied a procedure for checking the correctness of such assignments starting from the observed integrals of the signals of  $^{13}\text{C}$  NMR spectra, set up in previous works on ethene/4M1P<sup>3d</sup> and ethene/norbornene copolymers.<sup>20</sup>

The analysis of the spectra of the copolymers provides a certain number of peak integrals, each peak corresponding to one

or more signals. For each peak, on the basis of the assumption that the area of a signal is proportional to the population of the carbons generating that signal, we wrote a linear equation describing the observed (normalized) integral as a function of the unknown molar fractions. For each copolymer composition, we generated a set of linear equations whose variables were chosen among the molar fractions (see Supporting Information). A number of stoichiometric constraints reduced the number of independent variables. Least-squares fitting of the set of equations provided the best solution for the unknown molar fractions.

We applied the above procedure to two copolymers quite differing in comonomer content (5.70 and 53.27 mol %, respectively). Tables 3 and 4 compile the observed and calculated values of the normalized peak areas for each distinct and

**Scheme 3.**  $^1\text{H}\text{-}^{13}\text{C}$  Long-Range Correlation of Branch  $\alpha\alpha\text{-Methylene Carbon Atom of a PY Sequence}$



**Figure 8.** HSQC (a) and HMBC (b) spectra of a P/4M1P copolymer with 15.74 mol % (run 6 in Table 1). The box shows the expanded region of methylene groups, and \*\* refers to the new assigned signal.

Table 2. Chemical Shift Assignments for Propene/4-Methyl-1-pentene Copolymer

Chemical Structure	Carbon		Compositional Sequence	Steric Sequence	Chemical Shift (ppm)
	$S_{\text{oc}}$	PP	YPPY		45.05–44.97
			PPPY		44.48
			PPPP	<i>mmmrmm</i>	44.58
		<i>mmrrm</i>		44.24	
				<i>mmmmmm</i>	44.10
		PY	YPY+YPYP		42.49–42.28
			PPYP+PPYY		41.90
		YY	YYYY		40.05
			PYY□		39.90
CH <sub>2</sub> (sc)	methylene	PYP		44.20	
		PYY		43.89	
		YYY	PYYY□	43.75	
			YYYYY	43.65	
	$T_{\text{pp}}$	PYP	PYP	29.34	
		PYY	PPYY□	29.29	
			YPYY□	29.11	
		YYY	PYYYP	29.03	
			PYYYY	28.93	
			YYYYY	28.85	
Propene CH	$T_{\text{pp}}$	P	P	26.49–25.87	
CH (sc)	methine	Y	Y	23.50	
CH <sub>3</sub> (sc)	methyl	Y	PYY	21.51	
			YYYYY	21.44	
			PYP	21.24	
			PYY	21.10	
	$P_{\text{pp}}$	PPP	PPPPP	<i>mmmm</i>	19.68
				<i>mmmr</i>	19.40
				<i>mmrr</i>	18.87
				<i>mrrm</i>	17.64
			YPPP□	19.59	
		YPP	PYPPP	19.55	
			YPPP□	19.43–19.40	
YPY	PYPY□	19.31			
	YYPY□	19.11			

measurable group of signals, along with the sequences from which the signals arise. Although in the spectrum the signals of the different compositional and stereosequences of the methyl of propene in the region between 19.67 and 17.54 ppm have been

distinguished and assigned, owing to a partial overlap of their integrals we had to sum up their contributions in one equation. The same was made for a few sequences belonging to  $\alpha$ -methylene of propene and those of the methylenes of the branch,



Table 3. Least-Squares Fitting of  $^{13}\text{C}$  NMR Signals for Sample 4

sequence	chemical shift	normalized peak area		independent variables				
		obsd	calcd	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_7$
$f(\text{P})$	19.67–17.64	−0.061	−0.058	−1	0	0	0	0
$2f(\text{Y})$	21.50–21.10	0.116	0.116	2	0	0	0	0
$f(\text{Y})$	23.50	0.055	0.058	1	0	0	0	0
$f(\text{P})$	26.49–25.87	−0.055	−0.058	−1	0	0	0	0
$f(\text{Y})$	29.34–28.85	0.058	0.058	1	0	0	0	0
$f(\text{YY})$	39.90	0.007	0.008	1	−0.5	0	0	0
$f(\text{PPYP}) + f(\text{PPYY})^a$	41.90	0.088	0.087	0	1	0	−2	0
$f(\text{PYPY}) + f(\text{YYPY})^a$	42.49–42.28	0.013	0.012	0	0	0	2	0
$f(\text{YYY})$	43.75	0.000	0.000	1	−1	1	0	0
$f(\text{PPPP}) + f(\text{PPPY}) + f(\text{PYP}) + f(\text{PYY})^a$	43.89–44.58	−0.058	−0.060	−1	0.5	−1	0	−1
$f(\text{YPPY})$	44.97	0.015	0.013	0	0	0	0	1
best-fitting molar fraction				0.0571	0.1038	0.0489	0.0079	0.0108

$R^2 = 0.9976$   
 $\nu_1 = f(\text{Y}); \nu_2 = f(\text{PY}); \nu_3 = f(\text{PYP}); \nu_4 = f(\text{YPY}); \nu_7 = f(\text{YPPY})$

<sup>a</sup> The determination of the coefficients of the independent variables is reported in the Supporting Information.

Table 4. Least-Squares Fitting of  $^{13}\text{C}$  NMR Signals for Sample 10

sequence	chemical shift	normalized peak area		independent variables				
		obsd	calcd	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_7$
$f(\text{P})$	19.67–17.64	−0.537	−0.541	−1	0	0	0	0
$2f(\text{Y})$	21.50–21.10	1.142	1.121	2	0	0	0	0
$f(\text{Y})$	23.50	0.543	0.560	1	0	0	0	0
$f(\text{P})$	26.49–25.87	−0.540	−0.541	−1	0	0	0	0
$f(\text{Y})$	29.34–28.85	0.540	0.560	1	0	0	0	0
$f(\text{YY})$	39.90	0.334	0.350	1	−0.5	0	0	0
$f(\text{PPYP}) + f(\text{PPYY})^a$	41.90	0.228	0.241	0	1	0	−2	0
$f(\text{PYPY}) + f(\text{YYPY})^a$	42.49–42.28	0.166	0.168	0	0	0	2	0
$f(\text{YYY})$	43.75	0.266	0.266	1	−1	1	0	0
$f(\text{PPPP}) + f(\text{PPPY}) + f(\text{PYP}) + f(\text{PYY})^a$	43.89–44.58	−0.534	−0.534	−1	0.5	−1	0	−1
$f(\text{YPPY})$	44.97	0.061	0.061	0	0	0	0	1
best-fitting molar fraction				0.5412	0.4265	0.1335	0.0903	0.0581

$R^2 = 0.9975$   
 $\nu_1 = f(\text{Y}); \nu_2 = f(\text{PY}); \nu_3 = f(\text{PYP}); \nu_4 = f(\text{YPY}); \nu_7 = f(\text{YPPY})$

<sup>a</sup> The determination of the coefficients of the independent variables is reported in the Supporting Information.

Table 5. Triad Least-Squares Fitting for P/4M1P Copolymer Samples

run	Y (mol %)	triad						tetrad		
		PPP	PPY	YPY	PYP	PYY	YYY	PPPP	PPPY	YPPY
4	5.70	0.847	0.088	0.008	0.049	0.006	0.002	0.814	0.066	0.011
5	9.92	0.739	0.139	0.016	0.067	0.037	0.004	0.701	0.077	0.031
6	15.74	0.629	0.177	0.028	0.091	0.0517	0.022	0.579	0.101	0.038
8	35.88	0.312	0.244	0.072	0.078	0.232	0.062	0.225	0.176	0.034
9	43.00	0.198	0.265	0.077	0.120	0.179	0.160	0.116	0.164	0.050
10	54.12	0.108	0.241	0.089	0.126	0.168	0.267	0.049	0.119	0.061
11	60.75	0.095	0.219	0.091	0.142	0.116	0.337	0.040	0.108	0.055
12	67.21	0.042	0.172	0.098	0.133	0.102	0.451	0.010	0.062	0.054

falling in the spectral region between 44.48 and 43.89 ppm. For each item we report the coefficients of the independent variables considered. The best fitting molar fractions and the total

discrepancy function are given at the bottom of the tables. Thus, the present level of assignments has led to the determination of five independent molar fractions, i.e., all triads and some tetrads.

The tables show that, not only for the simplest spectrum of the sample at low comonomer content but also for the more complicated spectrum of the sample richer in comonomer, the differences between the observed and calculated values of the normalized peak areas are quite low.

In Table S, the triad and tetrad distributions for selected P/4M1P copolymers in a wide range of compositions are reported as obtained from the above procedure. A full description at the triad level is shown along with only a partial description at the tetrad level. Worth noting is that, although most tetrads have been safely assigned, only part of the information contained in the spectra can be fully exploited due to the overlap of several peaks. Indeed, the fact that the two pairs of tetrads  $\overline{\text{PYY}}\square$  and  $\overline{\text{YPY}}\square$  cannot be distinguished explains the absence of the  $\overline{\text{YY}}$ - and  $\overline{\text{PY}}$ -centered tetrads whose linear equations are strictly connected to the  $\overline{\text{PYY}}\text{P}$  and  $\overline{\text{YPY}}\text{P}$  molar fractions (see  $\nu_5$  and  $\nu_6$  in Supporting Information). This fact results in a limited estimate of the compositional tetrads. Such a level of microstructural description corresponds to the present state of the interpretation of the  $^{13}\text{C}$  NMR spectra in terms of sequence composition and is obviously open to further extensions with the improving in the interpretation of the spectra.

## CONCLUSIONS

We have examined the complete  $^{13}\text{C}$  NMR spectra of a series of propene/4-methyl-1-pentene copolymers prepared with *rac*-EBTHI at various comonomer contents. Starting from a limited number of available certain assignments, we succeeded in the complete  $^{13}\text{C}$  NMR assignment of such a family of copolymers. Our assignment allowed for the full description of the copolymers at the triad level. Although the complete description at the tetrad level could not be achieved so far, several sequences even longer than tetrads could be assigned and quantified as well. Heteronuclear correlated 2D NMR spectra were of great help in verifying and confirming the whole set of assignments. Through such experiments we solved the main difficulty, namely, the overlap of the signal from the methylenes of 4M1P with that of the  $\alpha\alpha$ -methylenes of the PPPP tetrad.

Besides, we have applied a best-fitting procedure for computing the molar fractions which defines the microstructure of these copolymers, utilizing the observed areas of the assigned  $^{13}\text{C}$  NMR signals and accounting for the stoichiometric requirements of the chain. The good agreement between the observed and calculated values of the sequence molar fractions is a clear evidence of the correctness of the assignment we have proposed. Although the complete description at the tetrad level could not yet be achieved, several sequences even longer than tetrads could be assigned and quantified as well. From now on, a route for achieving the quantitative determination of the microstructure of P/4M1P copolymers is thus available and could potentially allow for the successive determination of the copolymerization statistics of different catalysts and account for the macroscopic properties of the copolymers produced.

## EXPERIMENTAL SECTION

**General Experimental Details.** All experiments and manipulations involving air-sensitive compounds were carried out under dry nitrogen atmosphere in glovebox or by using standard Schlenk line techniques. Methylaluminoxane (MAO) (10 wt % as toluene solution, Crompton) was used after removing all volatiles and drying the resulting

powder at 50 °C for 3 h in vacuum (0.1 mmHg). Toluene was dried and distilled from sodium under a nitrogen atmosphere. Nitrogen and propene gases were dried and deoxygenated by passage over columns of  $\text{CaCl}_2$ , molecular sieves, and BTS catalysts.

**Propene/4-Methyl-1-pentene Copolymerizations.** A series of propene and 4-methyl-1-pentene copolymerizations were performed at 30 °C in a 250 mL glass reactor equipped with a magnetic stirrer by *rac*-(EBTHI)ZrCl<sub>2</sub>-MAO at  $[\text{Al}]/[\text{Zr}]$  molar ratio of 3000. A range of  $[\text{P}]/[\text{Y}]$  feed ratios as wide as possible was investigated. Polymerization time and catalysts varied to keep 4-methyl-1-pentene conversion below 6%.

**Nuclear Magnetic Resonance (NMR).** For  $^{13}\text{C}$  NMR, about 100 mg of copolymer was dissolved in  $\text{C}_2\text{D}_2\text{Cl}_4$  in a 10 mm tube. HDMS (hexamethylidisiloxane) was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 spectrometer operating at 100.58 MHz ( $^{13}\text{C}$ ) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90° pulse angle; 64K data points; acquisition time 5.56 s; relaxation delay 20 s; 3K–4K transient. Proton broad-band decoupling was achieved with a 1D sequence using *bi\_waltz\_16\_32* power-gated decoupling.

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

Two-dimensional NMR parameters: 90° pulse widths for  $^1\text{H}$  and  $^{13}\text{C}$  were 9.15 and 14.00  $\mu\text{s}$ , respectively; relaxation delay, 2.0 s; gHSQC experiments were carried out with a delay of 1.92 ms corresponding to a  $^1J_{\text{CH}} = 130$  Hz, for the creation of antiphase magnetization; 1.04 kHz as spectral width in the  $^1\text{H}$  dimension and 6.04 in the  $^{13}\text{C}$  dimension. Data were zero filled and weighted with a shifted sine bell function before Fourier transformation.

gHMBC experiments, with a 2-fold low pass J-filter, to suppress one-bond correlations, were carried out with a delay of 125 ms for the evolution of long-range coupling and delays corresponding to  $^1J_{\text{CH}}$  values of 110 and 150 Hz, for the creation of the antiphase magnetization. Spectral width was 1.04 kHz in the  $^1\text{H}$  dimension and 6.04 kHz in the  $^{13}\text{C}$  dimension. Data were zero filled and weighted with a sine bell 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  $3.3 \times 10^6$  g/mol were used.

## ASSOCIATED CONTENT

**Supporting Information.** Linear equations adopted for checking the correctness of the assignments in the present article. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ACKNOWLEDGMENT

This study was supported by Regione Lombardia, project no. 1336-VEGAPACK, 2009–2010. A. C. Boccia acknowledges the project FIRB n. RBIP062ZAM\_002 “ELASTORAD”. Thanks are due to Mr. Giulio Zannoni, who has carefully carried out the

1D NMR spectra. The authors express their gratitude to Dr. Lucia Zetta and Dr. Dino R. Ferro for their ever valuable and generous contributions. Thanks are due to Dr. Laura Boggioni for her helpful contribution to the revision.

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