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Propene−Norbornene Copolymers. Toward a Description of Microstructure at Triad Level Based on Assignments of ^{13}C NMR Spectra

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ABSTRACT: A procedure for the quantitative determination of the molar fractions of the stereosequences defining the microstructure of a propene−norbornene (P−N) copolymer from ^{13}C NMR spectra has been set up. This method utilizes the observed peak areas of the ^{13}C signals and takes into account the consistency between peak areas and the stoichiometry of the copolymer chain. With the support of homonuclear ^{1}H−^{1}H and heteronuclear ^{1}H−^{13}C NMR techniques, by guessing assignments of unknown signals, and by discarding inconsistent hypotheses, an extension of signal assignments is made possible. This procedure, which allows for a quantitative analysis of copolymer sequences as accurate as possible, has been applied to the analysis of the ^{13}C NMR spectra of a number of P−N copolymers prepared with catalyst precursors *rac*-Et(Indenyl)$_2$ZrCl$_2$ (**1**) and *rac*-Me$_2$Si(2-Me-Indenyl)$_2$ZrCl$_2$ (**2**). A complete description of the microstructure at triad level, including 1,3- and 2,1-propene insertions, has been attempted. New signals have been assigned such as those of the carbons of propene in the alternating triad $NP_{12}N$ and of norbornene in tetrad $NP_{12}NP_{12}$, as well as the signals of P_β methyl groups in triad $NP_{12}P_{12}$ adjacent to a variable number of P_{12} units all in isotactic relationship and those of the $S_{\alpha\gamma}$ methylene of a 1,3 propene inserted unit in the $NP_{13}P_{12}$ and of the methyl carbon atom of central monomer in $P_{21}P_{12}N$ and $NP_{21}P_{12}$. Although the goal of determining all the triads has not been achieved, an estimate of the molar fractions of the major sequences with a standard deviation on the order of 2−4% has been obtained. The quantitative determination of copolymer microstructure will allow one to clarify the P−N copolymerization mechanism.

Introduction

The discovery of metallocene-methylaluminoxane based catalysts[1] brought to advances in the synthesis of new classes of polymers. Among them the ethylene−norbornene (E−N) copolymers[2−4] are of great interest since they are amorphous materials with high transparency, high glass transition temperatures, and good chemical and heat resistance. Moreover, they have good processability by conventional methods and have been developed to commercial products. It was expected that investigation of propene−norbornene (P−N) copolymers would lead to even more exciting materials given the possibility to modulate regiospecificity and tacticity of propene homosequences. However, P−N copolymerization has been scarcely studied, probably owing to the difficulty of interpreting the ^{13}C NMR spectra of such copolymers.[5−9]

^{13}C NMR spectroscopy is surely the most powerful method for polymer microstructural investigations. However, P−N copolymer spectra are even more complex than those of E−N copolymers for the presence in the polymer chain of the possible regio- and stereoplacements of propene units and of the two stereogenic carbons per norbornene unit. Moreover, their chemical shifts as those of E−N copolymers do not obey straightforward additive rules, owing to the bicyclic nature of the norbornene structural units. Thus, based on the experience in elucidating the ^{13}C NMR spectra of E−N copolymers,[3] our group has accepted the challenge of assigning the ^{13}C NMR spectra of P−N copolymers.[6,7] ^{13}C NMR spectra and DEPT experiments, comparison of the chemical shifts of P−N copolymers with those of E−N copolymers, and ab initio theoretical ^{13}C NMR chemical shifts, combined with RIS statistics of the P−N chain, gave detailed indications for the ^{13}C NMR assignment of copolymers with isolated N units.[6,7]

Our continuous interest in finding catalysts and polymerization conditions which would make catalytic activities, norbornene content, and molar masses suitable for a development of these materials[8] brought us to synthesize P−N copolymers with different catalysts and compare them. We thought that the 2-methyl substitution on indenyl, which limits the chain transfer in propene homopolymerization, could serve for obtaining P−N copolymers with molar masses suitable for standard processing techniques. Comparison of the spectra of copolymers prepared with *rac*-Me$_2$Si(2-Me-Indenyl)$_2$ZrCl$_2$ with those by *rac*-Et(Indenyl)$_2$ZrCl$_2$ revealed the need of a more detailed microstructural analysis of such copolymers by ^{13}C NMR.

In the present work we have examined the complete ^{13}C NMR spectra of a number of P−N copolymers, prepared with catalysts *rac*-Et(Indenyl)$_2$ZrCl$_2$ (**1**) and *rac*-Me$_2$Si(2-Me-Indenyl)$_2$ZrCl$_2$ (**2**) having various norbornene contents. Our investigations were based on the following points: (i) the comparison of ^{13}C NMR spectra of P−N copolymers of various composition prepared with metallocenes **1** and **2**; (ii) a methodology for the quantitative analysis of copolymer sequences as accurate as possible; (iii) two-dimensional NMR techniques, including homonuclear ^{1}H−^{1}H and heteronuclear ^{1}H−^{13}C experiments. Starting from the available certain assignments and taking into account the consistency between peak areas and the stoichiometric requirements of the copolymer chain, we have set up a procedure for the determination of the different sequences of P−N copolymers. This method can be used to guess assignments of unknown signals and to verify the new assignments by discarding inconsistent hypotheses, thus allowing one to further extend the assignments. Correlated 2D NMR spectra were also of great help in verifying and confirming the whole set of assignments of ^{13}C propene and norbornene resonances depending on comonomer sequences. As a result, a more complete assignment of the ^{13}C spectra of P−N copolymers

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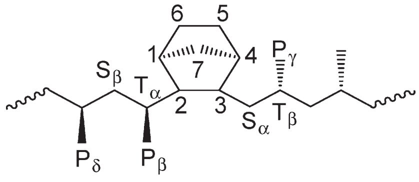


Figure 1. Schematic representation of a regular P–N copolymer chain (*PPNPP*) along with the numbering of carbon atoms used. The methyls of the two propene consecutive monomer units are in erythro as in an isotactic polypropene chain as well as in erythro relationship with the norbornene unit.

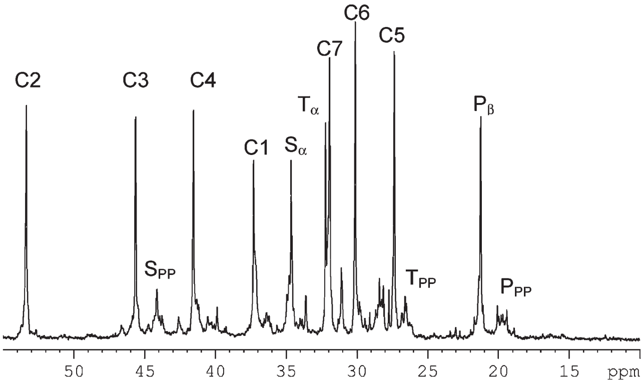


Figure 2. ^{13}C NMR spectrum of a P–N copolymer obtained by **1** ([N]/[P] = 0.22, f_N = 0.41).

will be reported. Although the full assignment at triad level has not been achieved, the methodology reported allows us to quantify the most informative triads as well as some longer sequences. This analysis will give us insights into the P–N copolymerization mechanisms, as will be reported in a forthcoming paper.[10]

P–N Copolymer Microstructure and Previous ^{13}C NMR Assignments. Previous studies have shown that norbornene in metallocene catalyzed copolymerization is enchained by 2,3-*exo*–cis addition.[11] A section of a P–N copolymer chain (*PPNPP*) in which norbornene can be considered isolated from other norbornene units is shown in Figure 1 along with the numbering of carbon atoms used. The methyls of two consecutive propene units are in erythro as in an isotactic polypropene chain as well as in erythro relationship with the norbornene unit.

The ^{13}C NMR spectrum of a copolymer obtained with **1** and containing about 40 mol % of *N* is displayed in Figure 2 along with the main peak assignments.[3] The signals of methylenes C6 and C5 appear at 30.10 and 27.34 ppm, respectively, while the C7 methylene appears at 31.91 ppm. The signals of methynes C1 and C4 appear at 37.17 and 41.32 ppm, respectively, while those of C3 and C2 are at 45.40 and 53.32 ppm, respectively. In addition to the primary, secondary, and tertiary carbon atoms of polypropene, the methyl P_β carbon atom was assigned to the resonance at 21.24 ppm.

Shiono[12] succeeded in the synthesis of P–N copolymers with high *N* content up to 71 mol % with catalyst (*ter*-BuNSiMe$_2$Flu)TiMe$_2$ (**3**) activated by Me$_3$Al-free methylaluminoxane (dried MAO). They observed several signals for each carbon due to the different comonomer sequences and stereoisomers of the norbornene unit. The signals around 26–30.4 and 30.26–35.42 ppm were tentatively assigned to carbons C5/C6 and C7, respectively.[13] In particular, a broad resonance with several peaks at 31.2–32.1 ppm which disappeared in the spectrum of polynorbornene could be assigned to the C7 carbon of the norbornene unit in alternating and/or norbornene dyad sequences. The signals at 33.3–35.4 ppm, visible also in the spectrum of polynorbornene, were assigned to *NNN* triads. The signals at about 36.4–41.4 ppm and 43–53 ppm were therefore tentatively assigned to C1/C4 and C2/C3 carbons, respectively. Signals between 48 and 53 ppm were assigned to C2/C3 carbons of *NNN* triads. Moreover, the signals between 12.0 and 17.0 ppm, which appear at high *N* content, were assigned to a methyl of a propene unit connected to norbornene.

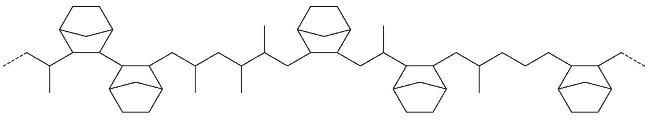


Figure 3. Typical random P–N copolymer chain (the sequence reads ... $NP_{13}P_{12}NP_{12}NP_{21}P_{12}P_{12}NNP_{12}$... since we consider the metal at the extreme left side).

The spectra studied by Shiono and those studied by us are very different for the norbornene content of the copolymers and for the stereospecificity of catalysts **3** and **1** giving syndio- and isotactic propene homosequences, respectively. In this paper we will focus on the elucidation of P–N copolymers with mid-low *N* content synthesized with C_2 symmetric metallocenes and thus giving mainly isospecific P homosequences.

A General Method for the Description of P–N Copolymers Based on the Analysis of Their ^{13}C NMR Spectra at Triad Level. Here we propose a general scheme to describe the microstructure of P–N copolymers at triad level on the basis of the assignments and the peak area measurements of their ^{13}C NMR spectra. This scheme includes: (i) definition of the possible triads composing the copolymer chain, (ii) use of NMR techniques to assign new signals, and (iii) a best-fitting procedure to determine the copolymer microstructure.

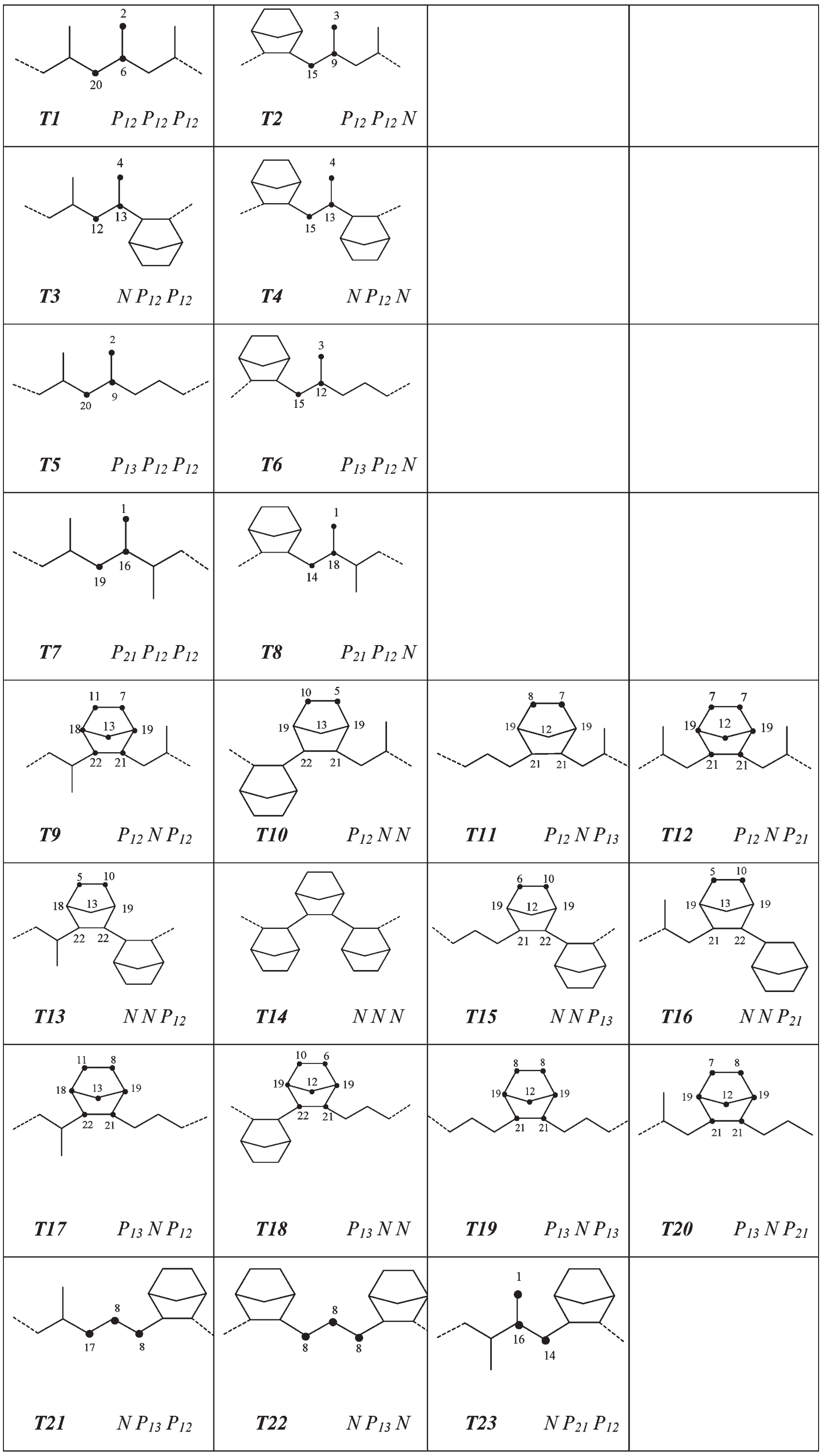
Triad Definitions. The P–N copolymer chain sketched above (Figure 3) has a typical random copolymer sequence distribution that we shall describe at triad level, for the moment ignoring differences in tacticity.

Propene *P* may be present in the copolymer chain in the forms P_{12}, P_{13}, and P_{21}. Thus, we have four monomer units (*M*): in the order, P_{12}, *N*, P_{13}, and P_{21}. On the basis of previous works on P–N copolymerization,[6,8] we assume that units P_{13} and P_{21} may be inserted only after *N*. We further assume that *N* cannot enter after P_{21}. Therefore, there are only nine diads: $P_{12}P_{12}$, $P_{12}N$, NP_{12}, NN, NP_{13}, NP_{21}, $P_{13}P_{12}$, $P_{13}N$, and $P_{21}P_{12}$. To be clear, diads $P_{12}P_{13}$, $P_{12}P_{21}$, $P_{13}P_{13}$, $P_{13}P_{21}$, $P_{21}N$, $P_{21}P_{13}$, and $P_{13}P_{13}$ are not considered (it is possible that in the case of a high *P* content P_{21} enters also after P_{12}, so that also diad $P_{12}P_{21}$ must be included, but here we do not consider this case). Under our assumptions, there are 23 possible triads, depicted in Chart 1. Because of the asymmetry of the bonds between *N* and P_{12} (or P_{21}), in general two diads M_1M_2 and M_2M_1 are not equivalent. In the chart, each triad $M_1M_2M_3$ is depicted as $M_3M_2M_1$, i.e. running from right to left (the catalyst metal ideally being bound to the extreme left side of the chain).

In Chart 1, to each atom of the central monomer M_2 we attach a code number representing the signal (or group of signals) assigned to that atom of M_2 in the environment of triad $M_1M_2M_3$ according to the current assignments. Since the present status of the assignments is far from being at the complete triad level, the same code may occur in two or more triads. The attribution of each signal code will be described in one of the following sections.

Two Dimensional NMR Techniques. Extension of signal assignments has been possible with the support of two-dimensional NMR techniques, including homonuclear

Chart 1. Possible Triads of a Random P−N Copolymer Chain.[a]



[a] Each triad $M_1M_2M_3$ is depicted as $M_3M_2M_1$, i.e., running from right to left (the catalyst metal ideally being bound to the extreme left side of the chain).

$^1H-^1H$ and heteronuclear $^1H-^{13}C$ experiments. First of all, DEPT experiments allow us to distinguish between primary, secondary, and tertiary carbons. We have acquired DEPT 135 experiments which show negative peaks for methylene groups against positive peaks for methyl and methyne groups; we distinguish methyl from methyne groups since we have shown that they appear in different regions of the spectra.[6] The comparison of chemical shifts of P−N copolymers with those of propene homopolymers allows to assign signals of *PPP* triads, while the comparison with shifts of prevailingly alternating P−N copolymers allows us to assign signals of *NPN* triads.

Then, the copolymer microstructure was investigated in details by high temperature two-dimensional NMR techniques with the aim to extend the ^{13}C chemical shift assignments to unknown resonances depending on the comonomer sequences or to confirm, at the same time, the ^{13}C chemical shift assignments previously determined.

A set of copolymers was extensively investigated by applying the heteronuclear $^1H-^{13}C$ experiments namely gHSQC (gradient-assisted heteronuclear single quantum coherence) and $^1H-^{13}C$ gHMBC experiments (gradient-assisted heteronuclear multiple bond correlation) together with the not reported homonuclear $^1H-^1H$ data.[14]

The gHSQC experiment provides correlations between the resonances of ^1H and ^{13}C atoms having one-bond scalar couplings ($^1J_{CH}$), thus highlighting all the direct one bond proton−carbon correlations. This experiment produces a final spectrum in which each peak correlates the chemical shifts of ^1H with those of the directly bonded ^{13}C.

Once assigned all the direct $^1H-^{13}C$ connectivities, the next step for a complete and unambiguous resonance assignment consists in the acquisition of the $^1H-^{13}C$ gHMBC experiments. This experiment detects with great sensitivity all the long-range connectivities between protons and carbons that are two or three bonds away providing information on the chemical environments. This technique allows us to assign new resonances depending on the comonomer sequences at triad level, identifying structure fragments in the copolymer.

Set of Equations. The analysis of the spectra provides a certain number of peak integrals, each peak corresponding to one or more signals. For each peak we can write a linear equation describing the observed (normalized) integral as a function of the unknown molar fractions. For each copolymer sample, the association given in Chart 1 between ^{13}C NMR signals and chemical environment of the carbons originating the signals will be used to generate a set of equations whose best-fitting solution determines the microstructure of the copolymer chain. This is based on the assumption that the area of a signal is proportional to the population of the carbons generating that signal. Thus, the normalized peak area NPA(i) of a signal due to carbon C_i contained n_i times in the central monomer unit of sequence S represents the molar fraction $f(C_i)$ of carbon C_i:

$$\begin{aligned}\mathrm{NPA}(i) &= \mathrm{area}(i)/\mathrm{total\ area} = f(C_i)\\ &= \mathrm{number}(C_i)/\mathrm{total\ number\ of\ atoms}\\ &= n_i \\ &\quad \times \mathrm{number}(S)/[7 \times \mathrm{number}(N) + 3 \\ &\quad \times \mathrm{number}(P)]\\ &= n_i f(S)/[7f(N) + 3f(P)]\\ &= n_i f(S)/[4f(N) + 3] \end{aligned} \tag{1}$$

being $f(N) + f(P) = 1$.

In particular, the normalized peak areas of all methyl carbons and of all CH carbons are given by:

$$\mathrm{NPA(CH_3)} = [f(P_{12}) + f(P_{21})]/[4f(N) + 3] \quad \text{and}$$

$$\mathrm{NPA(CH)} = [f(P_{12}) + f(P_{21}) + 4f(N)]/[4f(N) + 3], \quad \text{respectively}$$

Their difference Δ may be used to calculate $f(N)$:

$$\Delta = \mathrm{NPA(CH)} - \mathrm{NPA(CH_3)} = 4f(N)/[4f(N) + 3]; \quad \text{hence} \tag{2}$$

$$f(N) = 3/4\Delta/(1 - \Delta) \quad \text{and} \tag{3}$$

$$4f(N) + 3 = k = 3/(1 - \Delta) \tag{4}$$

Therefore, in the present approach to assign the spectra at the triad level, general equation 1 relates NPA's and triad molar fractions and may be expressed as:

$$k(\mathrm{NPA}(i)) = \Sigma_j\, n_{ij} f(T_j) \tag{1'}$$

where the sum is extended to triads j contributing to signal i and n_{ij} is the number of carbons C_i contained in the central residue of the triad.

Finally, stoichiometric relationships and molar fraction normalization are used to reduce the number of independent variables. On the basis of our initial assumptions, there are 8 stoichiometric relationships among the 23 triads, besides normalization:

$$\begin{aligned}&f(P_{12}P_{12}N) = f(NP_{12}P_{12}) + f(P_{13}P_{12}P_{12}) + f(P_{21}P_{12}P_{12}) \quad \text{or}\\ &\mathbf{T5} = \mathbf{T2} - \mathbf{T3} - \mathbf{T7}\end{aligned} \tag{a}$$

$$\begin{aligned}&f(P_{12}NP_{12}) + f(NNP_{12}) + f(P_{13}NP_{12}) = f(NP_{12}P_{12}) + f(NP_{12}N) \quad \text{or}\\ &\mathbf{T9} = \mathbf{T3} + \mathbf{T4} - \mathbf{T13} - \mathbf{T17}\end{aligned} \tag{b}$$

$$\begin{aligned}&f(NP_{13}P_{12}) = f(P_{13}P_{12}P_{12}) + f(P_{13}P_{12}N) \quad \text{or}\\ &\mathbf{T21} = \mathbf{T5} + \mathbf{T6} = \mathbf{T2} - \mathbf{T3} + \mathbf{T6} - \mathbf{T7}\end{aligned} \tag{c}$$

$$\begin{aligned}&f(NP_{21}P_{12}) = f(P_{21}P_{12}P_{12}) + f(P_{21}P_{12}N) \quad \text{or}\\ &\mathbf{T23} = \mathbf{T7} + \mathbf{T8} \quad \text{or} \quad \mathbf{T8} = \mathbf{T23} - \mathbf{T7}\end{aligned} \tag{d}$$

$$\begin{aligned}&f(NP_{13}N) = f(P_{13}NP_{12}) + f(P_{13}NN) + f(P_{13}NP_{13}) + f(P_{13}NP_{21}) \quad \text{or}\\ &\mathbf{T20} + \mathbf{T18} = \mathbf{T22} - \mathbf{T17} - \mathbf{T19}\end{aligned} \tag{e}$$

$$\begin{aligned}&f(P_{12}NP_{12}) + f(P_{12}NN) + f(P_{12}NP_{13}) + f(P_{12}NP_{21})\\ &\quad = f(P_{12}P_{12}N) + f(NP_{12}N) + f(P_{13}P_{12}N) + f(P_{21}P_{12}N) \quad \text{or}\\ &\mathbf{T10} + \mathbf{T11} = \mathbf{T2} + \mathbf{T6} + \mathbf{T23} - \mathbf{T7} - \mathbf{T3} - \mathbf{T12} + \mathbf{T13} + \mathbf{T17}\end{aligned} \tag{f}$$

$$\begin{aligned}&f(NNP_{21}) = f(P_{12}NN) + f(P_{13}NN) \text{-} f(NNP_{12}) - f(NNP_{13}) \quad \text{or}\\ &\mathbf{T16} + \mathbf{T15} = \mathbf{T10} + \mathbf{T18} - \mathbf{T13}\end{aligned} \tag{g}$$

$$\begin{aligned}&f(NP_{13}P_{12}) + f(NP_{13}N) = f(P_{12}NP_{13}) + f(NNP_{13}) + f(P_{13}NP_{13}) \quad \text{or}\\ &\mathbf{T11} + \mathbf{T15} = \mathbf{T2} - \mathbf{T3} + \mathbf{T6} - \mathbf{T7} - \mathbf{T19} + \mathbf{T22}\end{aligned} \tag{h}$$

Finally, the normalization equation may be expressed as:

$$\mathbf{T1} + 4\mathbf{T2} - \mathbf{T3} + 2\mathbf{T4} + 3\mathbf{T6} - \mathbf{T7} + \mathbf{T10} + \mathbf{T14} + \mathbf{T18} + 2\mathbf{T22} + 3\mathbf{T23} = 1 \tag{i}$$

We have chosen as independent variables **x** the molar fractions of the following 14 triads: **T1**, **T2**, **T3**, **T4**, **T6**, **T7**, **T10**, **T12**, **T13**, **T14**, **T17**, **T19**, **T22**, and **T23** (from x_1 to x_{14} in this order).

Then, relationships a−d will determine dependent triads **T5**, **T8**, **T9**, and **T21**, while relationships e-h should provide triads **T11**, **T15**, **T16**, **T18**, and **T20**.

In the case of the copolymers currently examined, triad *NNN* (**T14**) is usually absent, so the number of independent variables reduces to 13.

In principle the above relationships allow one to express the set of eqs 1′ as

$$k(\mathrm{NPA}(i)) - c_{0i} = \sum_{j=1}^{13} c_{ij}x_j \qquad (1'')$$

and least-squares fitting of about 24 eqs 1″ with 13 variables should provide a complete triad description of the microstructure.

We note that eq 3 could be used to further reduce by one the number of independent variables. However, it is more correct to allow for some error in the estimate of $f(N)$ and to add eq 3 to the set of fitting equations without reducing the number of variables. This requires that factor $k = 4f(N) + 3$ be recalculated from $f(N)$ and the best-fitting procedure iterated until convergence.

Results and Discussion

Here, we present examples of the analysis of ^{13}C NMR spectra of copolymers prepared with the two catalysts *rac*-Et(Indenyl)$_2$-ZrCl$_2$ (**1**) and *rac*-Me$_2$Si(2-Me-Indenyl)$_2$ZrCl$_2$ (**2**). The complete spectra of two copolymer samples prepared with **1** and **2** are displayed in Figure 4, parts a and b, respectively. First of all, we are able to calculate the NPAs of total primary, secondary and tertiary carbons with the help of DEPT 135; an example is reported in the Supporting Information, Figure S1. By applying eq 3 we are able to estimate the norbornene content. Thus, we find that the P−N copolymer obtained by **1** with a [N]/[P] = 0.11 contains 34.0 mol % of norbornene. Considering the norbornene content and that the integrals of the resonances of norbornene in diads *NN* are rather small, this copolymer is mainly alternating. Conversely, the norbornene content of the P−N copolymer obtained by **2** with a [N]/[P] = 0.10 calculated by eq 3 is 16.0 mol %.

Worth noting, the inspection of the methyl region of Figure 4b reveals that the polypropene blocks are rather stereoirregular. This is surprising since catalyst **2** produces highly isotactic polypropene. This finding will be discussed in details in ref 10.

New Assignments by Two-Dimensional NMR. Examples of the application of two-dimensional NMR techniques to discriminate and unambiguously assign few resonances related to the comonomer sequences, only generically assigned before, are given below.

The HSQC and HMBC spectra[14] of a P−N copolymer, obtained with catalyst **1** (f_N = 0.34), are reported in Figure 5, parts a and b, respectively.

Figure 5a made it possible to assign the ^{1}H spectrum by analyzing the correlations with the main resonances previously assigned.[6,7]

The direct ^{1}H−^{13}C connectivities can be summarized as follows: (a) norbornene unit, C2 (δ_C = 53.5 ppm; δ_H = 1.23 ppm); C3 (δ_C = 45.7 ppm; δ_H = 1.51 ppm); C4 (δ_C = 41.7 ppm; δ_H = 1.98 ppm); C1 (δ_C = 37.2 ppm; δ_H = 2.11 ppm); C7 (δ_C = 31.92 ppm; δ_H = 0.88 and 1.30 ppm); C6 (δ_C = 30.3 ppm; δ_H = 1.08 and 1.43 ppm); C5 (δ_C = 27.5 ppm; δ_H = 1.1 and 1.43 ppm); (b) propene unit, CH$_3$ (mmmm) (δ_C = 19.7 ppm; δ_H = 0.82 ppm); CH$_2$ (δ_C = 44.11 ppm; δ_H = 0.80 and 1.20 ppm); CH (δ_C = 26.47 ppm; δ_H = 1.51 ppm). Moreover, the S_α carbon atom shows two distinct cross-peaks, (δ_C 34.61 ppm; δ_H 0.69 and 1.67 ppm) one for each magnetically unequivalent proton: indeed, one is *syn* and the other one is *anti* to the CH$_3$ group, so they undergo a different shielding.

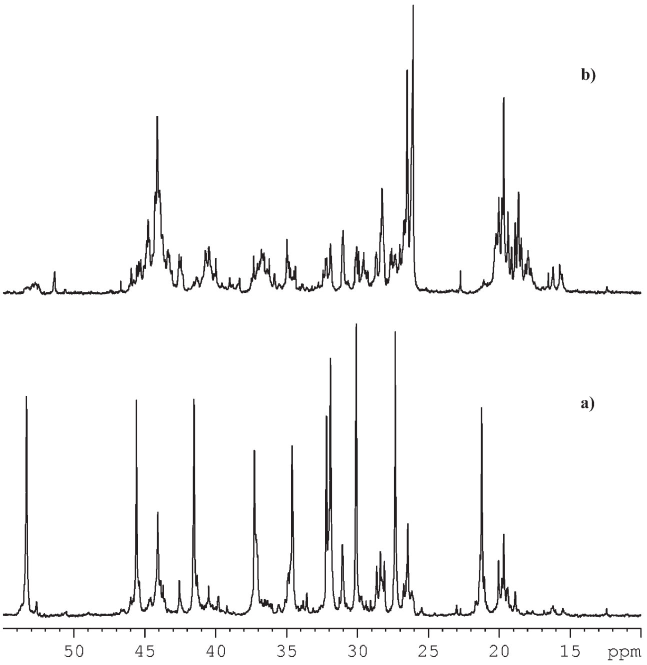


Figure 4. Complete spectra of two copolymer samples prepared with *rac*-Et(Indenyl)$_2$ZrCl$_2$ (**1**): (a) [N]/[P]$_{\mathrm{feed}}$ = 0.11, f_N = 0.34) and *rac*-Me$_2$Si(2-Me-Indenyl)$_2$ZrCl$_2$ (**2**) (B) [N]/[P]$_{\mathrm{feed}}$ = 0.10, f_N = 0.12).

Here below we report the case of P_β methyl group as an example of the method successfully applied for the determination of unknown resonances at triad level. Up to now, the ^{13}C resonance at δ_C = 21.26 ppm (δ_H = 0.88 ppm) was assigned to the methyl group of a propene unit near a norbornene, not distinguishing between P_β in the $NP_{12}P_{12}$ and $P_{\beta\gamma}$ in the $NP_{12}N$ sequence.

Figure 6b shows the expanded plot of the HMBC spectrum of Figure 5b, in the 22.0 − 20.0 ppm range, containing the methyl group under investigation. Drawing a horizontal line at δ_C = 21.26 ppm, only three main resonances in the ^{1}H domain are crossed, namely δ_H = 0.69, 1.23, and 1.67 ppm. Analyzing a selected section of the HSQC spectrum in Figure 6a, it is possible to assign the above-reported protons to the respective carbon atoms. In details, the two protons centered at δ_H = 0.69 and 1.67 ppm were assigned to the S_α carbon atom at δ_C = 34.61 ppm while the proton at δ_H = 1.23 ppm is assigned to the C2 carbon atom of a *N* unit. These long-range correlations are expected for a methyl group of a propene unit in both the $NP_{12}N$ (**T4**) and the $NP_{12}P_{12}$ (**T3**) triads (see Chart 1). However, the methyl group 4 in a **T3** sequence can be excluded due to the absence of the expected long-range correlations with the CH$_2$ (S_β) protons (δ_C = 31.10 ppm; δ_H = 0.87 and 1.32 ppm, see Figure 5b) assigned as explained below. Therefore, based on these characteristic multiple-bond correlations, the cross-peak centered at δ_C = 21.26 can be unequivocally assigned to the $P_{\beta\gamma}$ methyl group of a propene unit in a **T4** triad.

By extracting single rows (columns) from the 2D spectrum of Figure 5b at the correspondent ^{13}C (^{1}H) chemical shifts and determining the long-range connectivities from the analysis of 1D spectra, the following resonances were attributed: (i) δ 28.12 ppm to the methylene carbons 8 in the **T21** triad, (ii) the signal at δ 28.68 ppm to methyne carbon 9 in the **T2** triad; (iii) the signal at 31.10 ppm to methylene carbon 12 in **T3**; and (iv) the signal at δ 34.91 ppm to the methyne carbon 16 in the **T7** triad. Two examples of these assignments

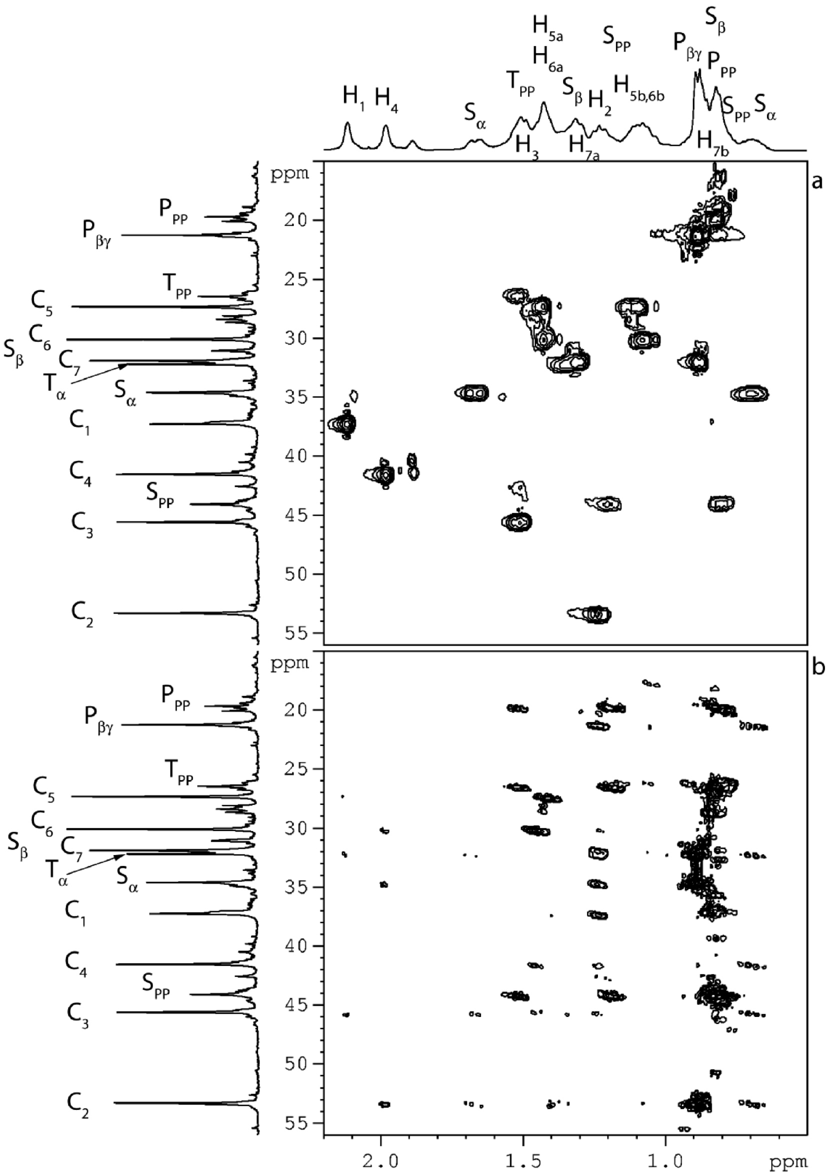


Figure 5. Main chain assignments determined by gHSQC (a) and gHMBC (b) spectra of the copolymer of a P−N copolymer obtained with catalyst **1** (f_N = 0.34).

are shown in the Supporting Information, Figures S2 and S3."

All these experiments confirm the assignments hypothesized and verified with our computing procedure.

Current Assignments. In this section we shall describe the level of assignment of the ^{13}C NMR spectra of P−N copolymers obtained in the present work. As we said earlier, the results are based on the previous assignments and on those discussed above, as well as on the application of a trial and error procedure, which consists in making hypotheses on new assignments of signals and in verifying the consistency of the hypotheses with the experimental intensities of the signals and the stoichiometric requirements of the copolymer chain. The current assignments are listed in Table 1.

Each item includes the signal code reported in Chart 1, the chemical shift range of the signal or of a group of signals, and a list of carbons contributing to those resonances, each with the corresponding triad. The grouping of more signals may be due to uncertainty in the assignments or to the insufficient separation of different areas. A further column reports the method used to achieve the assignment. A typical set of coefficients n_{ij} of eqs 1′, derived from Table 1, is presented in Table S1 in the Supporting Information.

Starting the analysis of the ^{13}C NMR spectrum from the right side, in Figure 7 and in Figure S4 in the Supporting Information, the resonances at 15.54, 16.22, and 16.34 ppm (code 1) are due to the methyl carbon atom of central monomer in $P_{21}P_{12}P_{12}$, $P_{21}P_{12}N$, and $NP_{21}P_{12}$, respectively. These signals have been assigned based on comparison with the signals $P_{21}P_{12}P_{12}$ in isotactic polypropene.[14,15] Thus, the normalized peak area of these signals corresponds to the sum of triads **T7** + **T8** + **T23** (Table 1). Therefore, in the first row of Table S1 the coefficient n_{1j} (eq 1′) of **T7**, **T8**, and **T23** is 1.

In the spectrum region from 17.80 to 19.83 ppm (code 2), the peaks of methyl carbon atoms of triads **T1** and **T5** occur.

At 20.08 ppm (code 3), the primary carbon atoms of the central monomer in $P_{12}P_{12}N$ (**T2**) and $P_{13}P_{12}N$ (**T6**) triads resonate.

The spectra of the copolymers obtained with catalysts **1** and **2** show significant differences in the following region ranging from 20.08 to 21.70 ppm (code 4). Catalyst **1**: the major peak at 21.26 ppm corresponds to the methyl of

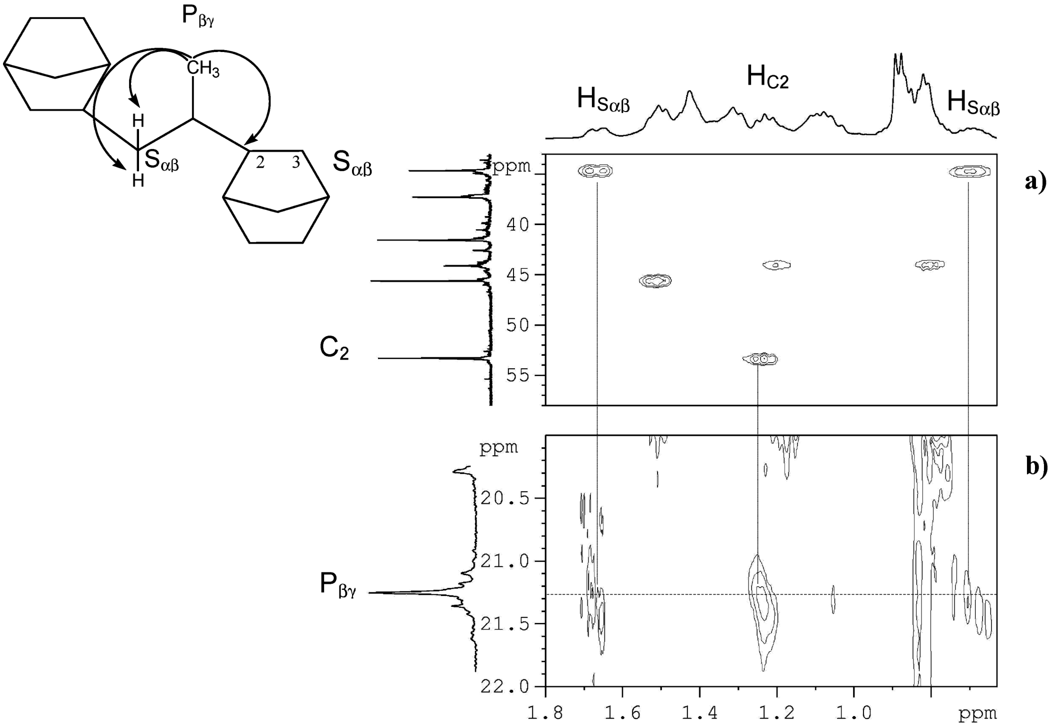


Figure 6. Expanded plot of the gHSQC spectrum of Figure 5a (a) and selected region from the gHMBC spectrum of Figure 5b in the proton chemical shift region between 1.8 and 0.6 ppm (b) of a P−N copolymer obtained with catalyst **1** (f_N = 0.34).

central monomer in triad $NP_{12}N$ (**T4**), while the spread neighboring signals arise from the methyl of triad $NP_{12}P_{12}$ (**T3**). Catalyst **2**: due to the low norbornene content the methyl signal of triad $NP_{12}N$ (**T4**) is barely visible, while a new signal appears at 20.25 ppm. We attribute this signal to the methyl of triad $NP_{12}P_{12}$ (**T3**) having different tacticity. This stereochemical shift agrees with the above-mentioned stereoirregularity of the polypropene blocks and may find a basis on previous considerations on the conformational origin of P−N copolymers,[16] namely that an upfield shift of the signal of carbon P_β should occur when it is in *racemic* relationship with carbon P_δ or with carbon C1 of N (see Figure 1 for nomenclature).

Code 5 corresponds to the signal at 25.45 ppm, tentatively assigned to the C5 norbornene carbon atom in the triads **T10**, **T13**, and **T16**. In the region between 26.15 and 26.77 ppm (code 6), there are the signals of the methyne carbon atom of **T1** and the signals of the C5 norbornene carbon atom of **T15** and **T18**.[3]

Between 26.80 and 27.45 ppm (code 7), one C5 norbornene carbon atom of **T9**, two C5 carbon atoms of **T12**, one C5 of **T11**, and one of **T20** resonate. In particular, the sharp peak at 27.36 ppm, which represents one of the seven major norbornene signals in the prevailingly alternating copolymer, has to be assigned to carbon C5 in the sequence $NP_{12}NP_{12}$ (the same argument holds below for carbons C1, C2, C3, C4, and C6).

The group of signals between 28.12 and 28.41 ppm (code 8) is due to the resonances of two CH_2 propene carbon atoms of **T21**, three CH_2 propene carbons of **T22**, and the C5 norbornene carbon atom in **T11**, **T17**, **T19**, and **T20**. Peak 28.68 ppm (code 9) has been assigned to the methyne carbon atom of propene in triads **T2** and **T5**.

The group of signals between 29.30 and 29.70 ppm (code 10) is due to the resonance of C6 norbornene carbon atom in the triads **T10**, **T13**, **T15**, **T16**, and **T18**. Between 29.72 and 30.20 ppm (code 11) there is a signal corresponding to the C6 carbon atom in triads **T9** and **T17**, while the sharp peak at 30.12 ppm is due to C6 of tetrad $P_{12}NP_{12}N$ and the group of signals between 30.20 and 31.31 ppm (code 12) is due to the C7 norbornene carbon atom in triads **T11**, **T12**, **T15**, **T18**, **T19**, and **T20**, the CH propene carbon atom of triad **T6**, and the CH_2 propene carbon atom of triad **T3**.

In the region between 31.93 and 32.21 ppm (code 13) signals of both propene and norbornene carbon atom are present. The signal centered on 31.93 ppm was previously assigned to the C7 norbornene carbon atom of a triad $P_{12}NP_{12}$ (**T9**).[6] We now assign the signal centered at 32.21 ppm to the CH propene carbon atom in the triad $NP_{12}N$ (**T4**). The other signals present in this region have been assigned to the propene CH carbon atom in the triad **T3** and to the C7 norbornene carbon atom in the triads **T10**, **T13**, **T16**, and **T17**.

At 33.60 and 33.90 ppm (code 14) the two small peaks have been assigned to the CH_2 propene carbon atom in the triads **T23** and **T8**, respectively.

The region between 34.64 and 35.12 ppm includes the resonances of the secondary propene carbon atom in the three different comonomer sequences $P_{12}P_{12}N$ (**T2**), $NP_{12}N$ (**T4**), and $P_{13}P_{12}N$ (**T6**) (code 15) and the signal of propene methyne in triads **T7** and **T23** at 34.91 ppm (code 16).

At 35.70 ppm (code 17) the $S_{\alpha\gamma}$ methylene of a 1,3 inserted propene unit in the $NP_{13}P_{12}$ triad (**T21**) is present.

In the region between 36.80 and 38.00 ppm (code 18) the signal of the C1 norbornene carbon atom in the three triads $P_{12}NP_{12}$ (**T9**), NNP_{12} (**T13**), and $P_{13}NP_{12}$ (**T17**) overlaps with the CH propene carbon atom signal in the triad $P_{21}P_{12}N$ (**T8**). The major peak at 37.30 ppm corresponds to carbon C1 of tetrad $P_{12}NP_{12}N$.

In the next region (code 19) there is a group of peaks due to the resonances of C4 norbornene carbon atom in the triads $P_{12}NP_{12}$ (**T8**), $P_{12}NN$ (**T10**), $P_{12}NP_{13}$ (**T11**), $P_{12}NP_{21}$ (**T12**), NNP_{12} (**T13**), NNP_{13} (**T15**), NNP_{21} (**T16**), $P_{13}NP_{12}$ (**T17**), $P_{13}NN$ (**T18**), $P_{13}NP_{13}$ (**T19**), and $P_{13}NP_{21}$ (**T20**) and to the

Table 1. Current Assignments of ^{13}C NMR Spectra of Random P−N Copolymers

signal code from chart 1	range (ppm)	carbons	triads	method used to achieve the assignment
1	15.45−16.80	**P**	**T7**	ref 15
		P	**T8**	16.22 ppm, this work: by fitting procedure and 2D NMR
		P	**T23**	16.34 ppm, this work: by fitting procedure and 2D NMR
2	17.80−19.83	**P**	**T1**	e.g., ref 1
		P	**T5**	e.g., ref 1
3	20.08	$\mathbf{P}_{\gamma}$	**T2**	this work: by fitting procedure
			T6	this work: by fitting procedure
4	20.08−21.70	**P**	**T3**	20.25 ppm, this work: by 2D NMR
		P	**T4**	21.26 ppm ($P_{\beta\gamma}$,) $NP_{12}NP_{12}$, this work: by 2D NMR
5	25.45	$\mathbf{C}_5$	**T10**	this work: by fitting procedure
			T13	this work: by fitting procedure
			T16	this work: by fitting procedure
6	26.15−26.77	**T**	**T1**	e.g., ref 1
		$\mathbf{C}_5$	**T15**	for comparison with ENN in ref 3
			T18	for comparison with ENN in ref 3
7	26.80−27.45	$\mathbf{C}_5$	**T9**	27.36 ppm $NP_{12}NP_{12}$, this work: by fitting procedure
			T11	this work: by fitting procedure
			T12	this work: by fitting procedure
			T20	this work: by fitting procedure
8	28.12−28.41	**S**	**T21**	this work: by fitting procedure and 2D NMR
		$\mathbf{C}_5$	**T11**	this work: by fitting procedure
		$\mathbf{C}_6$	**T17**	this work: by fitting procedure
			T19	for comparison with ENE in ref 3
			T20	this work: by fitting procedure
			T22	this work: by fitting procedure
9	28.68	**T**	**T2**	this work: by fitting procedure and 2D NMR
		$\mathbf{T}_{\beta\delta}$	**T5**	this work: by fitting procedure and 2D NMR
10	29.30	$\mathbf{C}_6$	**T10**	for comparison with ENN in ref 3
	29.70		**T13**	for comparison with ENN in ref 3
			T15	for comparison with ENN in ref 3
			T16	for comparison with ENN in ref 3
			T18	for comparison with ENN in ref 3
11	29.72−30.20	$\mathbf{C}_6$	**T9**	30.12 ppm $P_{12}NP_{12}N$, this work: by fitting procedure
			T17	this work: by fitting procedure
12	30.20−31.31	$\mathbf{C}_7$	**T11**	this work: by fitting procedure
			T12	this work: by fitting procedure
			T15	for comparison with ENN in ref 3
			T18	for comparison with ENN in ref 3
			T19	for comparison with ENE in ref 3
			T20	this work: by fitting procedure
		S	**T3**	31.10 ppm, this work: by fitting procedure and 2D NMR
			T6	this work: by fitting procedure
13	31.93−32.21	$\mathbf{T}_{\alpha}$	**T3**	ref 6
		$\mathbf{T}_{\alpha\beta}$	**T4**	ref 6
		$\mathbf{C}_7$	**T9**	ref 6
			T10	this work: by fitting procedure
			T13	this work: by fitting procedure
			T16	this work: by fitting procedure
			T17	this work: by fitting procedure
14	33.60−33.90	$\mathbf{S}_{\alpha\alpha}$	**T8**	this work: by fitting procedure
			T23	this work: by fitting procedure
15	34.64−35.12	**S**	**T2**	ref 6
			T4	this work: by fitting procedure and 2D NMR
			T6	ref 6
16	34.91	**T**	**T7**	ref 15
			T23	this work: by fitting procedure and 2D NMR
17	35.7	$\mathbf{S}_{\alpha\gamma}$	**T21**	this work: by fitting procedure
18	36.80−38.00	$\mathbf{C}_1$	**T9**	37.30 ppm $P_{12}NP_{12}N$, this work: by fitting procedure
			T8	this work: by fitting procedure
			T13	this work: by fitting procedure
			T17	this work: by fitting procedure
19	39.20−42.60	$\mathbf{C}_4$	**T9**	41.56 ppm of $NP_{12}NP_{12}$, this work: by fitting procedure
			T10	this work: by fitting procedure
			T11	this work: by fitting procedure
			T12	this work: by fitting procedure
			T13	this work: by fitting procedure
			T15	for comparison with ENN in ref 3
			T16	this work: by fitting procedure
			T19	for comparison with ENE in ref 3
			T20	this work: by fitting procedure
		S	**T7**	ref 15
20	43.65−44.63	**S**	**T1**	e.g., ref 1
			T5	e.g., ref 1
21	45.44−46.20	$\mathbf{C}_3$	**T9**	45.64 ppm of $NP_{12}NP_{12}$, this work: by fitting procedure

Table 1. Continued

signal code from chart 1	range (ppm)	carbons	triads	method used to achieve the assignment
			T10	this work: by fitting procedure
			T11	this work: by fitting procedure
			T12	this work: by fitting procedure
			T15	for comparison with ENN in ref 3
			T16	this work: by fitting procedure
			T17	this work: by fitting procedure
			T19	for comparison with ENE in ref 3
			T20	this work: by fitting procedure
22	49.00−55.70	C_3	**T13**	this work: by fitting procedure
			T15	for comparison with ENN in ref 3
			T18	for comparison with ENN in ref 3
		C_2	**T9**	53.36 ppm $P_{12}NP_{12}N$, this work: by fitting procedure
			T10	this work: by fitting procedure
			T13	this work: by fitting procedure
			T16	this work: by fitting procedure
			T17	this work: by fitting procedure

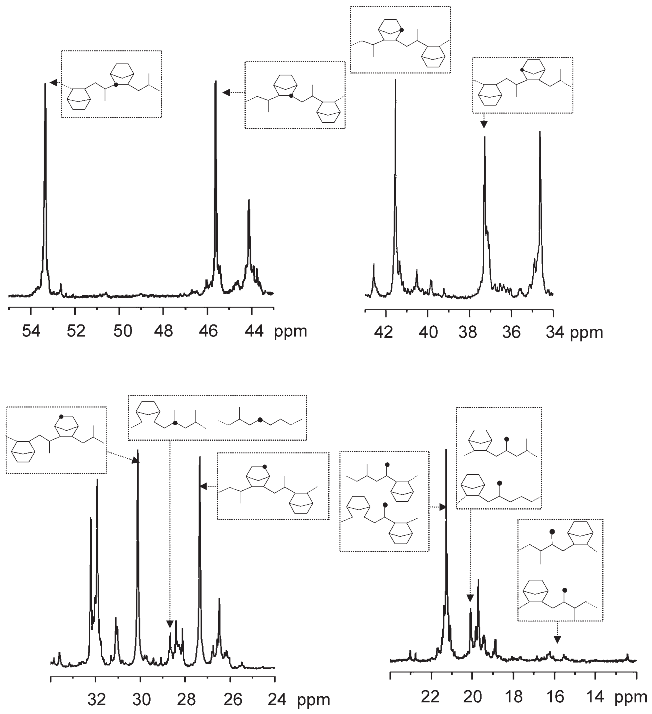


Figure 7. Expanded regions of ^{13}C NMR spectra of copolymer sample prepared with *rac*-Et(Indenyl)$_2$ZrCl$_2$ (**1**) ([N]/[P]$_{feed}$ = 0.11, f_N = 0.34).

CH propene carbon atom in the triad $P_{21}P_{12}P_{12}$. In particular, the sharp signal at 41.56 ppm has been assigned to C4 norbornene carbon atom in the sequence $NP_{12}NP_{12}$. Therefore, the NPA of this region correspond to the sum of triads **T9** + **2T10** + **2T11** + **2T12** + **T13** + **2T15** + **2T16** + **T17** + **2T18** + **2T19** + **2T20** + **T7.**

Between 43.65 and 44.63 ppm (code 20) the CH$_2$ signals occur of the sequences $P_{12}P_{12}P_{12}$ (**T1**) and $P_{13}P_{12}P_{12}$ (**T5**).

Finally in this region, the signals of C3 and C2 norbornene carbon atoms in the triads **T9**, **T10**, **T11**, **T12**, **T13**, **T15**, **T16**, **T17, T18, T19** and **T20** appear between 45.00 and 56.00 ppm (codes 21 and 22). Here, the peaks at 45.64 and 53.36 ppm are due to C2 of tetrad $P_{12}NP_{12}N$ and to C3 of tetrad $NP_{12}NP_{12}$, respectively.

Summarizing, below are highlighted some of the main novel assignments, displaced in Chart 2:

(1) the resonances at 16.22 and 16.34 ppm due to the methyl carbon atom of central monomer in $P_{21}P_{12}N$ (**T8**) and $NP_{21}P_{12}$ (**T23**), respectively;
(2) the signal at 20.05 ppm due to the methyl carbon atom (P_γ) of the central monomer in $P_{12}P_{12}N$ (**T2**);
(3) the signal at 21.26 ppm of the $P_{\beta\gamma}$ of alternating triad $NP_{12}N$ (**T4**);
(4) the signals from 21.05 to 21.94 ppm to P_β methyls in triad $NP_{12}P_{12}$ (**T3**) adjacent to a variable number of P_{12} units all in isotactic relationship;
(5) the signal at 20.25 ppm to the methyl of triad $NP_{12}P_{12}$ (**T3**) adjacent to a variable number of P_{12} units having different tacticity;
(6) the signal at 25.45 ppm to the C5 norbornene carbon atom of triad $P_{12}NN$ (**T10**);
(7) the signal centered at 32.21 ppm to the CH propene carbon atom in the triad $NP_{12}N$ (**T4**);
(8) the signals at 33.60 and 33.90 ppm to CH$_2$ propene carbon atom in the triads $NP_{21}P_{12}$ (**T23**) and $P_{21}P_{12}N$ (**T8**), respectively;
(9) the signal at 35.70 ppm to the $S_{\alpha\gamma}$ methylene of a 1,3 propene inserted units in the $NP_{13}P_{12}$ triad (**T21**).

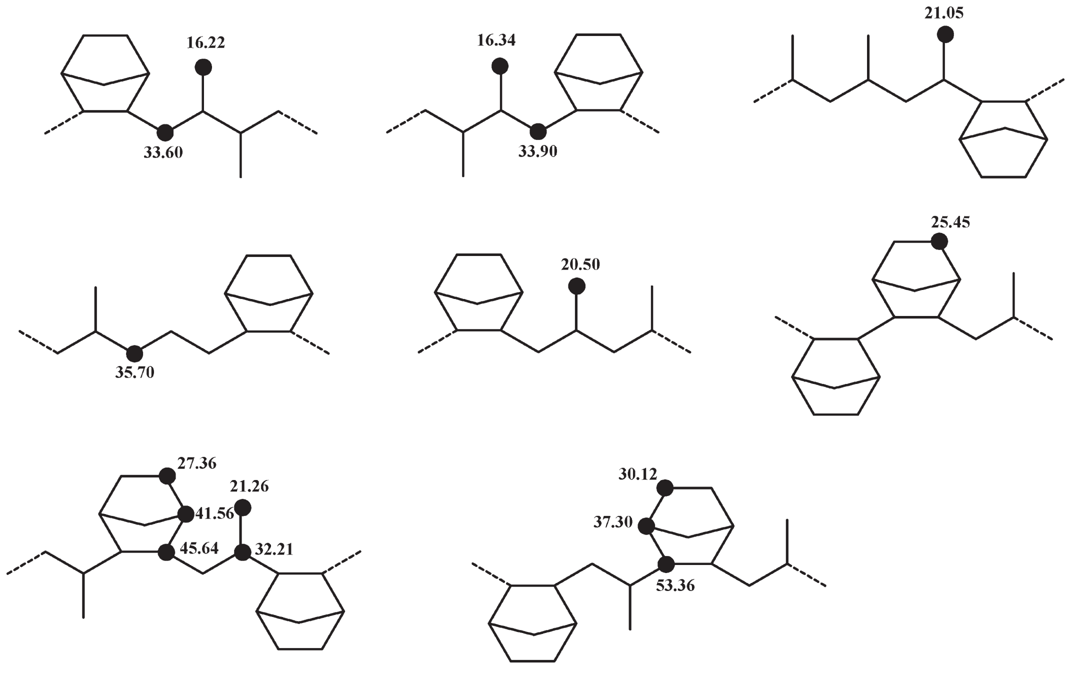
Analysis of ^{13}C NMR Spectra by the Procedure at Triad Level. On the basis of Table S1 of the Supporting Information, least-squares fitting of about 22 eqs 1″ with 13 variables should provide a complete triad description of the microstructure. In practice the examination of coefficients c_{ij} shows that the current assignments do not allow for a complete triad description. This is mainly due to the fact that the signals originated by *NN* diads are not resolved at triad level. First of all, we find that variable **T10** does not appear in any of eqs 1″, thus the independent variables reduce to 12 and relationships e−i only provide 5 combinations of the 6 triads **T10**, **T11**, **T15**, **T16**, **T18**, and **T20**.

Furthermore, we find that the coefficients of variables **T12**, **T17**, and **T19**, are linearly dependent, so that we can define the independent variable x_7 = **T17** + **T19** − **T12** and fit a set of equations with 10 independent variables.

Moreover, we measured the amounts of the triads containing the P_{21} defect directly from the spectra, the corresponding signals being well separated from the rest, in order to avoid some numerical difficulties in the least-squares fitting. Indeed, in the initial analysis of the spectra of some samples we observed vanishing or negative molar fractions of triads clearly evidenced by the spectra. This was probably due to the overlapping of spectral regions or residual errors in our assignment.

Thus, according to the first line of Table 2 and to stoichiometric relationship d, **T23** is taken as (proportional to) one-half of the NPA of the signal from 15.54 to 16.22 ppm (code 1). We further assume that triads $P_{21}P_{12}P_{12}$ (**T7**) and $P_{21}P_{12}N$

Chart 2. Main Novel Assignments



(**T8**), whose sum equals **T23**, are partitioned in the ratio **T7**/**T8** = f_P/f_N.

Such a procedure was used to analyze the ^{13}C NMR spectra of a number of P−N copolymers having N content ranging from 12 to 53 mol %, prepared with catalysts **1** and **2**.

Examples of the equations for the analysis of the spectra of two copolymers prepared with catalysts **1** and **2** are given in Tables 2 and 3, respectively. There are 8 independent variables, while **T23** and **T7** are treated apart. Details on the derivation of the coefficients of these tables may be found in the Supporting Information. Tables 2 and 3 compile the observed and calculated values of the datum (k NPA(i) − c_{0i}) for each distinct and measurable group of signals. For each item we report the coefficients c_{ij} of the independent variables considered. The best-fitting molar fractions and their standard deviations are given at the bottom of the table.

We observe that in Table 2 the estimated standard deviations of the molar fractions for the sample obtained with catalyst **1** are in the order of 2%. Table 3, related to data for the sample produced with catalyst **2**, reveals deviations on the order of 3−4%. These larger discrepancies may arise from the norbornene signals in the spectrum of the copolymer prepared with catalyst **2**, which are broader and smaller than those in the spectrum of the copolymer from catalyst **1**, owing to the lower norbornene content and to the increased stereo- and regioirregularity. The order of such discrepancies must induce caution in evaluating the significance of the small values of some molar fractions.

However, we can draw significant conclusions from the inspection of Table 4, where we collected the triad molar fractions estimated for two series of copolymers obtained with the two catalysts. In this table we present the most interesting triad molar fractions derived from the best fit independent variables by using the stoichiometric relations (a−i). Here, we only point out: the high value of triad $NP_{12}N$ in the alternating copolymer from **1** in contrast to the vanishingly low content of this triad from **2**; the persistently high content of $P_{12}P_{12}P_{12}$ even at high feed ratio in the series from **2**; the presence of triads containing propene misinsertions or regioerrors in greater amount in the series from **2** than in **1**. All these findings can be significant for mechanistic considerations.

Conclusions

We have presented an analytical procedure which utilizes the observed intensities of the assigned signals of ^{13}C NMR spectra for determining the molar fractions of the sequences defining the microstructure of a propene−norbornene copolymer at triad level. Differences in tacticity have been ignored but all the possible forms of propene insertion (P_{12}, P_{21}, and P_{13}) have been taken into account. Novel assignments have been achieved on the basis of hypotheses, verified by our computing procedure, in some cases supported by high temperature two-dimensional NMR techniques. Application of the procedure to a number of P−N copolymers prepared with two different catalysts allowed us to estimate the molar fractions of the triads with a standard deviation on the order of 2 to 4% depending on the catalyst used for the synthesis. Mechanistic implications of these analysis are presented in a forthcoming paper.[10] The extension of this method to samples prepared with catalysts leading to copolymers with different microstructure or with a very high norbornene content should lead to further assignments of NMR chemical shifts in longer norbornene blocks and to a thorough investigation of the P−N chain. On the other hand, the quantitative determination of the microstructure of these copolymers will allow one to progress in clarifying the polymerization mechanism.

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 nitrogen atmosphere. *rac*-$Me_2Si(2\text{-}Me\text{-}Indenyl)_2ZrCl_2$ was purchased from Boulder. Nitrogen and propene gases were dried and deoxygenated by passage over columns of $CaCl_2$, molecular sieves, and BTS catalysts. Norbornene was distilled from sodium and used as stock solution in toluene.

Table 2. Least-Squares Fitting of ^{13}C NMR Signals for Sample Produced with Catalyst *rac*-Et(Indenyl)$_2$ZrCl$_2$ (1) with a [N]/[P]$_{\text{feed}}$ = 0.11

			data		coefficients c_{ij} of independent variables							
					x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
signal code i	eq. i		obsd k NPA(i) − c_{0i}	calcd $\Sigma_j n_{ij} f(T_j)$	**T1**	**T2**	**T3**	**T4**	**T6**	**T13**	**T17 +** ***T19*** **−** ***T12***	**T22**
1	1	2**T23**[a]	0.3572		0	0	0	0	0	0	0	0
2	2	**T1 + T5**	0.2514	0.2374	1	1	−1	0	0	0	0	0
3	3	**T2 + T6**	0.0751	0.0862	0	1	0	0	1	0	0	0
4	4	**T3 + T4**	0.3023	0.2797	0	0	1	1	0	0	0	0
5	5	**T10 + T13 + T16**	−0.9817	−0.9829	−1	−4	1	−2	−3	1	1	−3
6	6	**T1 + T15 + T18**	−0.7543	−0.7392	0	−4	1	−2	−3	−1	−1	−1
7	7	**T9 + T11 + 2T12 + T20**	1.2658	1.2950	1	5	−1	3	4	0	−1	3
8	8	**T11 + T17 + 2T19 + T20 + 2T21 + 3T22**	1.1371	1.1346	1	7	−4	2	6	1	1	6
9	9	**T2 + T5**	0.0701	0.0811	0	2	−1	0	0	0	0	0
10	10	**T10 + T13 + T15 + T16 + T18**	−1.9377	−1.9477	−2	−8	2	−4	−6	0	0	−4
11	11	**T9 + T17**	0.2949	0.2760	0	0	1	1	0	−1	0	0
12	12	**T3 + T6 + T11 + T12 + T15 + T18 + T19 + T20**	0.1258	0.1325	0	1	0	0	2	0	−1	2
13	13	**T3 + T4 + T9 + T10 + T13 + T16 + T17**	−0.4819	−0.4271	−1	−4	3	0	−3	0	1	−3
14	14	**T23 + T8**	0.0199		0	0	0	0	0	0	0	0
15	15	**T2 + T4 + T6**	0.3245	0.3084	0	1	0	1	1	0	0	0
16	16	**T7 + T23**	0.0104		0	0	0	0	0	0	0	0
17	17	**T21**	0.0359	0.0286	0	1	−1	0	1	0	0	0
18	18	**T9 + T8 + T13 + T17**	0.3295	0.2797	0	0	1	1	0	0	0	0
19	19	**T7 + T9 + 2T10 + 2T11 + 2T12 + T13 + 2T15 + 2T16 + T17 + 2T18 + 2T19 + 2T20**	−1.5862	−1.5771	−2	−6	1	−3	−4	0	0	−2
20	20	**T1 + T5**	0.2097	0.2374	1	1	−1	0	0	0	0	0
21	21	**T9 + T10 + 2T11 + 2T12 + T15 + T16 + T17 + T18 + 2T19 + 2T20**	0.3524	0.3706	0	2	−1	1	2	0	0	2
22	22	**T9 + T10 + 2T13 + T15 + T16 + T17 + T18**	−1.6576	−1.6679	−2	−8	3	−3	−6	0	0	−4
23	23	$F_N = (3/4\ \Delta)/(1 - \Delta)$	−0.6577	−0.6487	−1	−3	1	−1	−2	0	0	−1
best-fitting molar fractions					0.2256	0.0693	0.0575	0.2222	0.0169	0.0037	0.0040	0.0168
standard deviation					0.018	0.018	0.021	0.020	0.018	0.008	0.017	0.013
R^2 = 0.9992												

[a] k = 4.356 and NPA = 0.0082.

Table 3. Least-Squares Fitting of ^{13}C NMR Signals for Sample Produced with Catalyst *rac*-Me$_2$Si(2-Me-Indenyl)$_2$ZrCl$_2$ (2) with [N]/[P]$_{\text{feed}}$ = 0.10

			data		coefficients *cij* of independent variables							
					x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
signal code *i*	eq *i*		obsd *k* NPA(*i*) − c_{0i}	calcd $\Sigma_j n_{ij} f(T_j)$,	**T1**	**T2**	**T3**	**T4**	**T6**	**T13**	**T17 + T19 − T12**	**T22**
1	1	2**T23**^{a}	0.0769		0	0	0	0	0	0	0	0
2	2	**T1 + T5**	0.5512	0.5876	1	1	−1	0	0	0	0	1
3	3	**T2 + T6**	0.1111	0.1156	0	1	0	0	1	0	0	0
4	4	**T3**	0.0133	0.0337	0	0	1	0	0	0	0	0
4	5	**T4**	0.0714	0.0060	0	0	0	1	0	0	0	0
5 + 6	6	**T1 + T10 + T13 + T15 + T16 + T18**	−1.4351	−1.3814	−1	−8	2	−4	−6	0	−4	−1
7	7	**T9 + T11 +** 2**T12 + T20**	1.1194	1.1170	1	5	−1	3	4	−1	3	1
8	8	**T11 + T17 +** 2**T19 + T20 +** 2**T21 +** 3**T22**	1.1810	1.2000	1	7	−4	2	6	1	6	1
9	9	**T5 + T2**	0.0937	0.1355	0	2	−1	0	0	0	0	0
10	10	**T10 + T13 + T15 + T16 + T18**	−1.8910	−1.9181	−2	−8	2	−4	−6	0	−4	−2
11	11	**T9 + T17**	0.0596	0.0397	0	0	1	1	0	0	0	0
12	12	**T3 + T6 + T11 + T12 + T15 + T18 + T19 + T20**	0.1594	0.1892	0	1	0	0	2	−1	2	0
13	13	**T3 + T4 + T9 + T10 + T13 + T16 + T17**	−0.9243	−0.9159	−1	−4	3	0	−3	1	−3	−1
15 + 16	14	**T2 + T4 + T6 +** 2**T23 + T7+ T8**	−0.0189	0.1216	0	1	0	1	1	0	0	0
17	15	**T21**	0.1705	0.0819	0	1	−1	0	1	0	0	0
18	16	**T8 + T9 + T13 + T17**	0.0860	0.0397	0	0	1	1	0	0	0	0
19	17	2**T10 + T13 + T9 +** 2**T11 +** 2**T12 +** 2**T16 +** 2**T15 +** 2**T18 +** 2**T19 +** 2**T20 + T7 + T17**	−1.6755	−1.7020	−2	−6	1	−3	−4	0	−2	−2
20	18	**T1 + T5 + T7**	0.6320	0.5876	1	1	−1	0	0	0	0	1
21	19	**T10 + T9 +** 2**T11 +** 2**T12 +** 2**T19 + T16 + T15 + T17 + T18 +** 2**T20**	0.2236	0.2161	0	2	−1	1	2	0	2	0
22	20	**T10 +** 2**T13 + T9 + T16 + T17 + T15 + T18**	−1.8877	−1.8784	−2	−8	3	−3	−6	0	−4	−2
23	21	$F_N = (3/4\,\Delta)/(1 - \Delta)$	−0.8660	−0.8311	−1	−3	1	−1	−2	0	−1	−1
best-fitting molar fractions					0.5367	0.0846	0.0337	0.0060	0.0310	0.000	−0.0300	0.0063
standard deviation					0.036	0.032	0.032	0.031	0.040	/	0.032	0.030
$R^2 = 0.9973$												

[a] $k = 4.627$ and NPA = 0.0212.

Table 4. Triads Molar Fractions of P−N Copolymers Obtained by Catalyst 1 and 2 at Different [N]/[P] Feed Ratios

			$P_{12}P_{12}P_{12}$	$P_{12}P_{12}N$	$NP_{12}P_{12}$	$NP_{12}N$	$P_{13}P_{12}P_{12}$	$P_{13}P_{12}N$	$P_{21}P_{12}P_{12}$	$P_{21}P_{12}N$	$NP_{13}P_{12}$	$NP_{13}N$	$NP_{21}P_{12}$
cat.	$f_{N(feed)}$	f_N	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**	**T8**	**T21**	**T22**	**T23**
1	0.10	0.34	0.226	0.069	0.058	0.222	0.000	0.017	0.012	0.006	0.017	0.017	0.018
1	0.18	0.41	0.129	0.050	0.035	0.260	0.006	0.025	0.009	0.006	0.031	0.025	0.015
1	0.30	0.45	0.086	0.043	0.026	0.298	0.011	0.004	0.007	0.005	0.014	0.047	0.012
1	0.35	0.45	0.103	0.039	0.015	0.286	0.017	0.001	0.007	0.005	0.018	0.052	0.012
2	0.05	0.12	0.635	0.061	0.029	0.000	0.000	0.039	0.032	0.005	0.039	0.000	0.037
2	0.09	0.16	0.537	0.085	0.034	0.006	0.018	0.031	0.032	0.006	0.049	0.006	0.038
2	0.12	0.15	0.564	0.068	0.029	0.025	0.008	0.036	0.031	0.006	0.044	0.002	0.037
2	0.22	0.16	0.513	0.103	0.051	0.000	0.043	0.035	0.009	0.002	0.078	0.001	0.010

Propene−Norbornene Copolymerizations. A series of propene and norbornene copolymerizations was performed in a Buchi BEP2000 autoclave with 1 L reactor by **1**-MAO and **2**-MAO at [Al]/[Zr] molar ratio of 2000 in toluene at 40 °C at 5 bar pressure of propene. A range of [N]/[P] feed ratios as wide as possible was investigated. Polymerization time varied to keep norbornene conversion below 10%.

^{13}C NMR. For ^{13}C NMR, about 100 mg of copolymer was dissolved in $C_2D_2Cl_4$ in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 Spectrometer operating at 100.58 MHz (^{13}C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90° pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3−4K 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}H and ^{13}C were 9.25 and 14.00 μs respectively; relaxation delay, 3.0 s.

gHSQC experiments were carried out with a delay of 1.92 ms corresponding to a $^1J_{CH} = 130$ Hz, for the creation of antiphase magnetization; 1.04 kHz as spectral width in the ^{1}H dimension and 7.04 in the ^{13}C dimension. Data were zero filled and weighted with a shifted sinebell function before Fourier transformation.

gHMBC experiments, with a 2-fold low pass J-filter, were carried out with a delay of 124 ms for the evolution of long-range coupling and delays corresponding to $^1J_{CH}$ values of 120 and 140 Hz, for the creation of the antiphase magnetization. Spectral width was 1.04 kHz in the ^{1}H dimension and 7.04 kHz in the ^{13}C dimension. Data were zero filled and weighted with a shifted sine bell function before Fourier transformation.

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Supporting Information Available: Text giving considerations leading to the stoichiometric relationships among triads equations, Table S1, showing the set of coefficients n_{ij} of equations derived from Table 1, text showing the determination of coefficients c_{ij} of independent variables in Table 2 and determination of coefficients c_{ij} of independent variables in Table 3, Figure S1, showing DEPT 135 of a N−P copolymer (f_N =0.22, [N]/[P] = 0.06), Figure S2, showing the ^{1}H NMR spectrum extracted from the HMBC spectrum of Figure 5b, correspondent to the CH(9) row (^{13}C range) at 28.68 ppm, Figure S3, showing the ^{1}H spectrum extracted from the HMBC spectrum of Figure 5b, correspondent to the Sβ row (^{13}C range) at 31.10 ppm, and Figure S4, giving expansions of Figure 7 showing region codes. This material is available free of charge via the Internet at http://pubs.acs.org.

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