Ab Initio Molecular Modeling of ^{13}C NMR Chemical Shifts of Polymers. 2. Propene−Norbornene Copolymers[†]

Paola Carbone, Massimo Ragazzi, Incoronata Tritto, Laura Boggioni, and Dino R. Ferro*

Istituto per lo Studio delle Macromolecole del CNR, Via E. Bassini,15 I-20133 Milano, Italy

Received August 2, 2002; Revised Manuscript Received November 25, 2002

ABSTRACT: A methodology based on ab initio DFT computations as well as on molecular mechanics has been devised for helping the elucidation of the microstructure of polymers through the interpretation of their ^{13}C NMR spectra and has been applied to the case of propene−norbornene (P−N) copolymers. In a first step, a rotational-isomeric-state model of the chain of these copolymers has been achieved. The results of molecular mechanics calculations on various model compounds were checked and corrected by means of ab initio DFT computations at high level of theory. In general, good agreement was found between the results obtained with Allinger's MM2 force field and with the quantum-mechanical method B3LYP/6-31G**. Then, theoretical ^{13}C chemical shifts for two basic compounds were obtained according to the GIAO (gauge including atomic orbitals) method, using a large basis set and Adamo and Barone's functional. The theoretical chemical shifts averaged over the RIS populations provided rather unambiguous indications for interpreting the ^{13}C NMR signals observed in spectra of isotactic (P−N) copolymers with mid-low norbornene content. Thus, only with the help of these calculations was it possible to achieve a first unambiguous assignment of each of the seven major N signals in the complex spectra of P−N copolymers. This methodology may turn out to be of general utility, in particular for those macromolecular systems where empirical relationships between conformation and chemical shifts are not available.

Introduction

Cycloolefin polymers and copolymers, which were made possible by the introduction of new classes of metallocene-based catalysts, may provide interesting materials endowed with good thermomechanical properties.[1] Since such properties depend greatly on the composition and the microstructure of the polymer chain, considerable effort has been devoted in the last years to elucidate the microstructure, in particular, of ethene−norbornene (E−N) copolymers, mainly on the basis of the interpretation of their ^{13}C NMR spectra.[2−7] It has also been shown that significant contributions to unravel the complex mass of information contained in the NMR spectra of E−N copolymers can be provided by the knowledge of the conformational characteristics of that chain. Indeed, the results obtained with a RIS model of the E−N copolymers[7b] suggested for the first time and proved the occurrence of the splitting of the signals of *meso* and *racemic* alternating NEN sequences. Second, the calculated changes in conformer populations at different distances from the norbornene ring allowed the authors to reach an unambiguous assignment of the ethylenic signals. Finally, the calculations qualitatively ascribed the origin of stereochemical shifts due to NN and NNN sequences to the ring deformations arising from steric hindrances. In the mentioned work,[7b] the indications on the chemical shifts were obtained by combining the conformer populations with empirical parameters representing shift effects, such as the so-called γ-*gauche* effect.[8,9] More recently, we found that advanced quantum-mechanical methods for computing ^{13}C NMR magnetic shieldings[10,11] may be applied successfully to reproduce stereochemical shifts of model compounds containing the norbornene moiety.[12] These methods are particularly useful to evaluate the effects of molecular arrangements for which no empirical data are available, as in the case of the distortions of the N ring. Thus, GIAO/DFT calculations utilizing the functional MPW1PW91 proposed by Barone and co-workers[13] confirmed independently the most recent assignments related to ENNE sequences of E−N copolymers.[12]

Much less attention has been paid so far to propene−norbornene (P−N) copolymers[14] in comparison with the E−N ones. In our laboratory a project has been started concerning the synthesis by metallocene-based catalysts, the determination of the microstructure by means of NMR spectroscopy, and eventually measurements of thermal properties of propene−norbornene copolymers. In this article we report on the results of molecular mechanics and ab initio computations on model compounds of the P−N copolymer chain. Molecular mechanics was utilized to set up a rotational-isomeric-state (RIS) model of an ideal P−N chain, partially following the previous work on E−N copolymers.[7b] The most stable conformers of some models were also subjected to energy minimization by means of ab initio quantum-mechanical calculations. One purpose was to test the validity of the RIS model with an independent theoretical method. Another, more important, purpose was to obtain a sufficient number of structures to be submitted subsequently to ab initio computations of the chemical shifts. The results obtained by combining the RIS populations with the conformational differences among ab initio chemical shifts here will be briefly compared with the experimental data of P−N copolymers synthesized with *rac*-Et(indenyl)$_2$ZrCl$_2$-based catalyst, which has been demonstrated to yield prevailingly isotactic and regioregular polypropene. A more detailed discussion will be presented in the article[15] adjoining this one (hereafter denoted as paper 2).

[†] Article 1 of this series was published in *Int. J. Quantum Chem.* (ref 12).

* Corresponding author: e-mail d.ferro@ismac.cnr.it.

10.1021/ma021247e CCC: $25.00

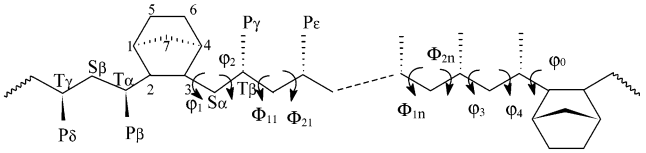

Figure 1. Schematic representation of a regular chain (N−$P_{n+2})_x$. The scheme shows the specific model of an isotactic ...*SS(S−R)RR*... copolymer, corresponding to configuration $c = c' = c'' = 1$.

Statistical Models

Here, on the basis of the behavior displayed by metallocene catalysts in the E−N copolymerization,[2,7,12] we represent a P−N copolymer by the ideal regioregular chain depicted in Figure 1, which shows the nomenclature adopted throughout the paper. The norbornene units are enchained 2,3-*exo*-*exo*.

The distinction C1/C4, C2/C3, and C6/C5 of the N ring atoms parallels the convention adopted in E−N copolymers.[2c,7c] Suffixes α, β, γ, ... of the propene carbons indicate the distance from the closest N ring. For brevity, we shall often indicate configuration $S-R$ of norbornene as L and configuration $R-S$ as D. For a segment of chain containing $n + 2$ propene units between two norbornenes, the conformation is defined by n pairs of dihedral angles (ϕ_{1i}, ϕ_{2i}, with i from 1 to n) representing normal polypropylene dyads, the pair of dihedrals (φ_1, φ_2) formed by the pseudo-dyad following the first N, the special dihedral φ_0 formed at bond Tα-C2, and the pair (φ_3, φ_4) representing the last polypropylene (PP) dyad preceding φ_0. The total (relative) configuration of such a segment is defined by (i) the configuration of the PP sequence, where we only consider the stereoregular *isotactic* ($c = 1$) and *syndiotactic* ($c = 2$) sequences; (ii) the relative configuration of Tα with respect to C2 [$c' = 1$, *meso*, e.g., Tα(S)−C2(S)−C3-(R); $c' = 2$, *racemic*, e.g., Tα(R)−C2(S)−C3(R)]; and (iii) the configuration of C3 relative to Tβ [$c'' = 1$, *meso*, e.g., C2(S)−C3(R)−Sα-Tβ(R); $c'' = 2$, *racemic*, e.g., C2(S)−C3(R)−Sα−Tβ(S)].

The statistics of a P−N copolymer with low−medium norbornene content was based on computations on model compounds PNP (**1**) and PPNP (**2**) shown in Figure 2. We compute the average conformation for a family of regular structures formed by the repetition of identical segments (N−P_{n+2}), each member of the family being characterized by n and by the configuration vector $\mathbf{c} = (c, c', c'')$. The total energy of such a chain is defined as

$$E_{\text{total}}(n,\mathbf{c}) = \sum_k \{ \sum_{i=1,n-1} [(E_{\text{PP}}\,(\phi_{1i},\phi_{2i};c)_k + E'_{\text{PP}}(\phi_{2i},\phi_{1i+1})_k] + E_{\text{PP}}(\phi_{1n},\phi_{2n};c)_k + E'_{\text{PP}}(\phi_{2n},\varphi_3)_k + E_{\text{PPNP}}(\varphi_3,\varphi_4,\varphi_0,\varphi_1,\varphi_2;\mathbf{c}) + E'_{\text{PP}}[(\varphi_2)_k,(\phi_{11})_{k+1}]\} \quad (1)$$

where index k represents one of the repeating segments, E_{PP} is the energy of a polypropylene dyad (*meso* or *racemic*), E'_{PP} is the interaction between two adjacent PP dyads, and E_{PPNP} representing the energy of the PPNP segment is a function of the five φ dihedrals as well as of the configuration vector **c**. As usual,[16] the average conformation of the chain and the associated properties are computed by assuming a discrete number of states for each dihedral. For the polypropylene moiety we adopted Suter and Flory's five-state model,[17] while for the PPNP segment the molecular mechanics calculations on model compounds **1** and **2** described below provided a statistical model based on 5 × 5 states for the "dyads" (φ_1, φ_2) and (φ_3, φ_4) and 3 states for φ_0. Moreover, we assumed that rotations (φ_1, φ_2) and (φ_3, φ_4) are uncorrelated, i.e., that the following additivity holds:

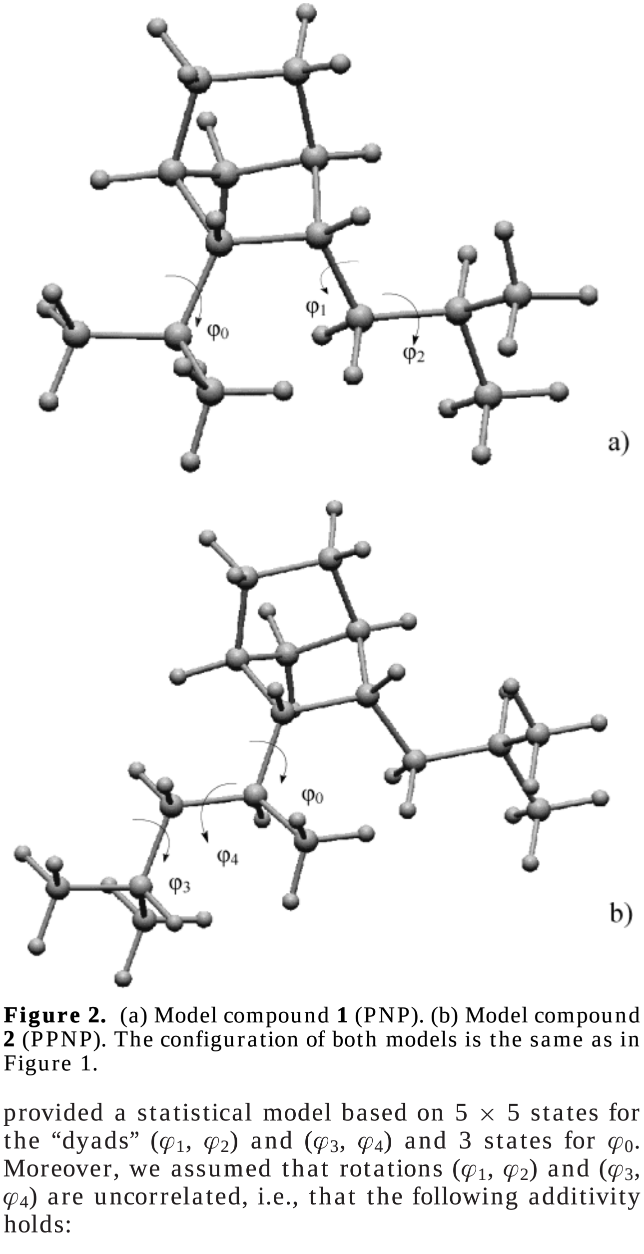

Figure 2. (a) Model compound **1** (PNP). (b) Model compound **2** (PPNP). The configuration of both models is the same as in Figure 1.

$$E_{\text{PPNP}}(\varphi_3,\varphi_4,\varphi_0,\varphi_1,\varphi_2;\mathbf{c}) = E_{\text{PPNP}}(\varphi_3,\varphi_4,\varphi_0,\varphi_1^0,\varphi_2^0;c,c') + E_{\text{PNP}}(\varphi_0,\varphi_1,\varphi_2;c',c'') - E_{\text{PNP}}(\varphi_0,\varphi_1^0,\varphi_2^0;c',c'') \quad (2)$$

Thus, the partition function Z(n,**c**) of the chain can be computed in terms of Suter and Flory's statistical weight matrices $\mathbf{U}_m''$, $\mathbf{U}_r''$, and $\mathbf{U}'$, corresponding to *meso* and *racemic* PP dyads and to the interdyad interaction, respectively,[17] and in terms of the Boltzmann factors of the PPNP moiety $w_{\text{PPN}}(i_3,i_4,i_0;c,c')$ and $w_{\text{PNP}}(i_0,i_1,i_2;c',c'')$. Let us define the 5 × 5 matrices:

$$\mathbf{W}_{\text{PP}} = \mathbf{U}'\cdot(\mathbf{U}_c''\cdot\mathbf{U}')^n \quad (3)$$

$\mathbf{W}_{\text{PPNP}}$, with elements $w_{\text{PPNP}}(i_3,i_2) =$

$$\sum_{i_4}\sum_{i_0}\sum_{i_1} w_{\text{PPN}}(i_3,i_4,i_0;c,c')\; w_{\text{PNP}}(i_0,i_1,i_2;c',c'') \quad (4)$$

and

$$\mathbf{W} = \mathbf{W}_{\text{PP}}\cdot\mathbf{W}_{\text{PPNP}} \quad (5)$$

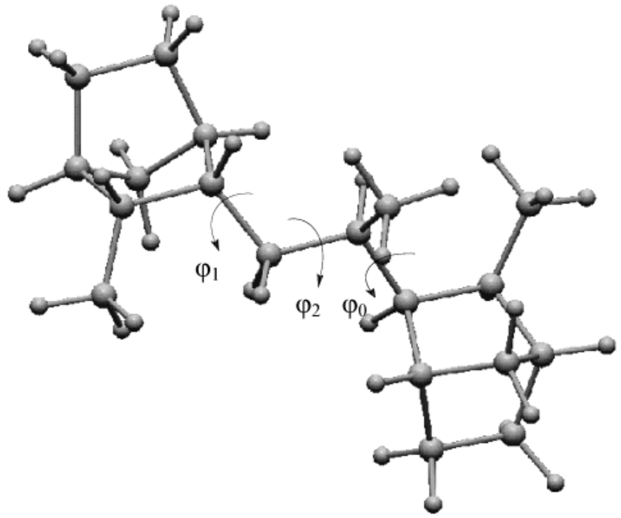

Figure 3. Model compound **3** (NPN). The configuration is $S-R/S/S-R$.

Then the partition function for a chain $(N-P_{n+2})_x$ can be expressed as

$$Z(n,\mathbf{c}) = (\mathbf{1})\cdot(\mathbf{W})^x\cdot(\mathbf{1})^T \qquad (6)$$

and the RIS populations at each bond are derived accordingly.

The chain of the alternating copolymer $(N-P)_x$ was treated separately, owing to the strong correlation between two adjacent N−P−N units. In this case, the statistical weights for the N−P−N segment of the chain $w_{NPN}(i_1,i_2,i_0;c',c'')$ were first derived from the energy maps of compound NPN (**3**), shown in Figure 3. For example, for $c' = c'' = 1$ a segment k is described by nine states $s_k = (i_1, i_2, i_0; 1, 1)_k$. To properly account for the interactions between two adjacents segments, it was necessary to compute the energy minima of compound Met−N−P−N−P−N−Met (**4**), which provided the interaction matrix

$$E_{int}(s_k,s_{k+1}) = E_{NPNPN}(s_k,s_{k+1}) - E_{NPN}(s_k) - E_{NPN}(s_{k+1}) \qquad (7)$$

and the corresponding Boltzmann factors $w_{int}(s_k,s_{k+1})$. The total energy is then defined as

$$E_{total} = \sum_k [E_{NPN}(s_k) + E_{int}(s_k,s_{k+1})] \qquad (8)$$

and if we define the matrix $\mathbf{W}$ with elements $w(s_k,s_{k+1}) = w_{NPN}(s_k)w_{int}(s_k,s_{k+1})$, the partition function of a chain made of $x + 1$ segments is

$$Z = (\mathbf{1})\cdot(\mathbf{W})^x\cdot(\mathbf{w}_{NPN})^T \qquad (9)$$

Methods

Molecular Mechanics. The first step of the work was the systematic search of the energy minima of model compounds **1**−**3**. Only one stereoisomer ($S-R$) was required for PNP, since the coefficients of w_{PNP} for the different combinations of c' and c'' are simply obtained by referring the dihedrals φ_0 and φ_2 to the appropriate β and γ methyl, respectively. For reasons analogous to the case of PNP, two stereoisomers are used for PPNP (S/L and R/L) and four for NPN ($L/S/L$, $L/R/L$, $L/S/D$, and $L/R/D$). According to the additivity assumption of eq 2, the calculations on PPNP were performed by varying (φ_3, φ_4) and φ_0, and setting (φ_1, φ_2) near the (φ_1^0, φ_2^0) conformation of minimum energy found in PNP for the given φ_0 value. The next step was the calculation of contour energy maps in the planes (φ_1, φ_2) (for **1** and **3**) and (φ_3, φ_4) (for **2**), for each φ_0 conformer. Each map was then divided in zones surrounding each energy minimum, and integration of the Boltzmann factor over each zone gave the statistical weights $w_{PNP}(i_0,i_1,i_2;c',c'')$, $w_{PPN}(i_3,i_4,i_0;c,c')$ and $w_{NPN}(i_1,i_2,i_0;c',c'')$.

The calculations were carried out using Allinger's force fields MM2 and MM3,[18] both in vacuo and with inclusion of chloroform solvent. The programs Macromodel[19] and CHAMP[20] were utilized for this purpose.

Quantum Mechanics. Ab initio computations, especially those based on high-level DFT (density functional theory), have proven to yield reliable values for atomic chemical shifts in terms of the isotropic magnetic shielding. A refined molecular geometry and a proper choice of the functional form are necessary to reach the precision required for the interpretation of complex NMR spectra and for the prediction of signals.[21] As in a previous paper,[12] here we adopted a three-step procedure for the calculations on the most stable and relevant conformers of model compounds **2** and **3**: (a) low-energy conformers (usually, within 10 kJ/mol from the minimum) were obtained with molecular mechanics, usually using force field MM3 with solvent $CHCl_3$;[19] (b) the conformers were subjected to a further energy minimization with the quanto-mechanical method (B3LYP/6-31G**) as implemented in Jaguar;[22] (c) magnetic shieldings for carbon atoms were computed according to GIAO (gauge including atomic orbitals)[11] as implemented in Gaussian98,[23] with a large basis set and with the functional proposed by Adamo and Barone:[12] in usual notation, this kind of computation is indicated by MPW1PW91/6-311+G(2d,p)//B3LYP/6-31G**, which is about the highest level of theory tractable with our computers for molecules of roughly 55 atoms. A slightly smaller basis set (6-31G**) was used only for model compound Met−N−P−N−P−N−Met (**4**, 77 atoms), considered for sake of comparison. The chemical shifts computed with these basis sets for the reference TMS carbon are 186.96 and 196.03 ppm, respectively, compared with the experimental value of 186.4 ppm.[24] It is to be pointed out, however, that in this kind of analysis the main interest is to reproduce the differences in chemical shifts for signals from various C atoms, rather than absolute values.

Results

RIS Populations. All computations yield three deep minima for dihedral φ_0. Hence, for each stereoisomer of compounds **1**−**3** three energy maps were computed corresponding to the three states i_0 of φ_0 (which we denote with the conventional symbols t, g', and g referred to values of φ_0 around 180°, −60°, and +60°). If we refer the φ_0 conformation to the *meso* ($c' = 1$) configuration S/L, the relative stability of the three states decreases in the order $t > g' > g$ (equivalent to the order $g > t > g'$ referred to R/L). The maps $E(\varphi_1,\varphi_2)$ and $E(\varphi_3,\varphi_4)$ in general show a low-energy area much restricted in comparison with a PP dyad and a smaller number of populated states. Nevertheless, these present a sufficient similarity with those of PP to maintain the 5 × 5 state scheme of PP. Thus, we classify them as

Table 1. Nonzero Statistical Weights $w_{PNP}(i_0,i_1,i_2;1,2)$ Obtained from MM2 Energy Maps of PNP at 100 °C; Conformational States and Average Angles Are Referred to Configuration *S*/*L*/*S*[a]

average conformation			states			$w_{PNP}(i_0,i_1,i_2;1,2)$[b]	
$\langle\varphi_0\rangle$	$\langle\varphi_1\rangle$	$\langle\varphi_2\rangle$	i_0	i_1	i_2	MM2	MM2corr
−161	−173	−173	1	1	1	0.4653	0.4653
−161	−176	−110	1	1	3	0.0204	0.0191
−165	−146	−63	1	2	4	0.0620	0.0580
−161	−156	61	1	2	5	0.0237	0.0138
−146	−80	−62	1	3	4	0.0124	0.0116
−157	74	−145	1	5	2	0.0004	0.0004
−78	−171	−172	2	1	1	0.2608	0.2608
−75	−154	−67	2	2	4	0.0539	0.0275
−75	−151	62	2	2	5	0.0177	0.0177
−80	−105	−174	2	3	1	0.0054	0.0054
−79	−79	−67	2	3	4	0.0504	0.0256
68	−172	−173	3	1	1	0.0254	0.0254
68	−154	62	3	2	5	0.0015	0.0014
64	−98	−67	3	3	4	0.0006	0.0006

[a] The equivalent states of configuration *S*/*L*/*R* can be obtained by exchanging the pairs of i_2 indexes (1, 4) (i.e., *t*, *g*) and (2, 3) (i.e., *t**, *g**). [b] Derived from MM2 energy maps by correcting on the basis of the differences between ab initio and MM2 values of the relative energies of some PPNP minima.

Suter and Flory's[17] states *t*, *t**, *g**, *g*, and $\bar{g}$, although in the following we shall use the angular values and the symbols denoting the conventional sense of rotation. The maps computed with MM3 show a narrower allowed area than those obtained with MM2. Inclusion of solvent produces modest shifts, on the order of 0.2 kcal/mol. For the sake of simplicity, we only present the results of MM2 without solvent and of MM3 with solvent; the other two combinations usually fall in between. Moreover, we analyzed in greater details the isotactic chain corresponding to configuration $c = c' = c'' = 1$, which represents the most probable idealization of the P−N copolymers being currently prepared in our laboratory, by means of metallocene-based catalysts such as *rac*-Et(indenyl)$_2$·ZrCl$_2$/MAO. For brevity, we shall report explicitly only the results strictly related to the conformer populations of our model of isotactic (P−N) copolymer. Further details may be found in the Supporting Information. Thus, the relative energies of the most stable minima of PNP computed with the two force fields are provided in Table S1. Here, Tables 1 and 2 list the nonzero values of the statistical weight matrices $w_{PNP}(i_0,i_1,i_2;1,2)$ and $w_{PPN}(i_3,i_4,i_0;2,1)$, computed at the temperature of 100 °C, while Figure 4 shows examples of PPNP energy maps.

Such matrices were then combined with the PP matrices into eqs 3−6 to compute the conformer populations of different chain models, representative of P−N copolymers with low−medium norbornene content (at least two propene units between adjacent norbornenes). The conformer populations computed for each dihedral of the isotactic copolymer $(P_4{-}N)_x$ are reported in Table 3, while comparison with different configurations can be done by inspection of Table S3. Finally, the behavior of the conformer populations in these isotactic chains vs parameter *n* is displayed in Table S4.

Concerning the alternating stereoregular copolymers $(P{-}N)_x$, Figure 5 shows the energy map $E(\varphi_1,\varphi_2)$ of NPN for state *t* of φ_0 and $c' = c'' = 1$, while Table 4 reports the statistical weights w_{NPN} $(i_1,i_2,i_0;1,1)$. The energies $E_{NPNPN}(s_k,s_{k+1})$ of **4** used to compute the interaction matrix $\mathbf{w}_{int}$ of eq 7 are supplied in the Supporting Information (see Table S5).

Table 2. Nonzero Statistical Weights $w_{PPN}(i_3,i_4,i_0;2,1)$ Obtained from MM2 Energy Maps of PPNP at 100 °C; Conformational States and Average Angles Are Referred to Configuration *R*/*S*/*L*[a]

average conformation			states			$w_{PPN}(i_3,i_4,i_0;2,1)$	
$\langle\varphi_3\rangle$	$\langle\varphi_4\rangle$	$\langle\varphi_0\rangle$	i_3	i_4	i_0	MM2	MM2corr[b]
175	−177	−159	1	1	1	0.3013	0.3013
167	122	−167	1	2	1	0.0095	0.0095
150	−55	−161	2	5	1	0.0209	0.0209
92	−179	−157	3	1	1	0.0139	0.0157
71	95	−160	4	3	1	0.0982	0.0858
67	−73	−157	4	5	1	0.0126	0.0126
−51	−177	−159	5	1	1	0.0055	0.0055
−65	124	−167	5	2	1	0.0043	0.0043
173	168	−78	1	1	2	0.3463	0.2829
156	−77	−72	2	5	2	0.0006	0.0005
104	170	−76	3	1	2	0.0167	0.0136
66	135	−80	4	2	2	0.0320	0.0142
−59	156	−80	5	2	2	0.0095	0.0078
173	171	68	1	1	3	0.0328	0.0302
164	120	64	1	2	3	0.0200	0.0184
145	54	66	2	4	3	0.0041	0.0038
72	132	64	4	2	3	0.0177	0.0163
66	53	64	4	4	3	0.0459	0.0181
−65	112	64	5	3	3	0.0083	0.0077

[a] The equivalent states of configuration *S*/*S*/*L* can be obtained by exchanging the pairs of i_3 indexes (1, 4) (i.e., *t*, *g*) and (2, 3) (i.e., *t**, *g**). The statistical weights of configuration *R*/*R*/*L* are given in Table S2. [b] Derived from MM2 energy maps by correcting on the basis of the differences between ab initio and MM2 values of the relative energies of some PPNP minima.

Ab Initio Energy Computations. The relative energies of the most significant conformers of PPNP computed ab initio are compared in Table 5 with the results of force-field calculations. The discrepancies between MM2 and ab initio energies were utilized to generate a third set of statistical weights w_{PNP} and w_{PPN} (see last column of Tables 1 and 2), besides the MM2 and MM3 sets.

In Table 6, we compare ab initio and force-field results for the stable conformers of stereoisomer *L*/*S*/*L* of **3**. A similar comparison concerning the lowest-energy conformers of stereoisomer *L*/*S*/*L*/*S*/*L* of **4** is given in Table S6. In the last two columns of Table 6 we also list the conformer populations computed for the NPN moiety of the alternating isotactic copolymer. One column reports the results derived from eq 9 on the basis of the MM2 statistics. The last column shows the conformer populations obtained by correcting the statistical weights w_{NPN} on the basis of the energy differences between ab initio and MM2 computations on model **3** and by partially correcting matrix $\mathbf{E}_{int}$ using the ab initio results of Table S6.

Ab Initio Chemical Shifts. Tables 7 and 8 show the ^{13}C NMR chemical shifts computed ab initio for the conformers of **2** and **3** listed in Tables 5 and 6, respectively. An analysis of these results in terms of the relationships between chemical shift and molecular structure will be presented elsewhere. Here, we only immediately notice that for all the conformers of Table 7 the chemical shift of C6 is greater than the value computed for C5 by more than 2 ppm: such a stereochemical shift is similar to the effect observed and computed for NN dyads in E−N copolymers.[12] Also evident are the large chemical shift splittings found for the two pairs of chemically equivalent carbons C2/C3 and C1/C4.

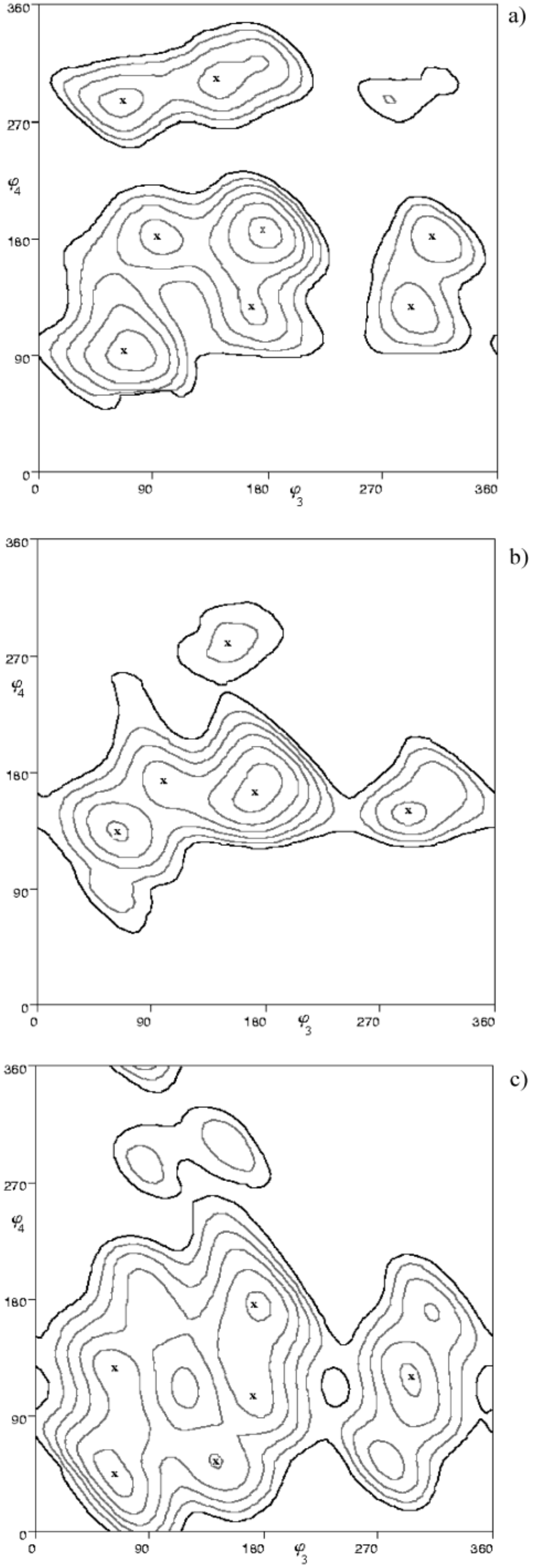

Figure 4. Energy maps $E(\varphi_3,\varphi_4)$ of PPNP for $c' = c'' = 2$ and for three states of dihedral φ_0: (a) $\varphi_0 = t$; (b) $\varphi_0 = g'$; (c) $\varphi_0 = g$. Contours separated by an energy difference of 5 kJ/mol.

Table 3. Conformer Distributions for the φ and ϕ Dihedrals of an Isotactic $(N{-}P_4)_x$ Chain (See the Definition of Dihedrals in Figure 1)

	conformer population		
dihedral	*t*	*g′*	*g*
φ_0	0.4458	0.4377	0.1164

	conformer population				
dihedral	*t*	*t**	*g**	*g*	$\bar{g}$
φ_1	0.5887	0.2832	0.1278		0.0002
φ_2	0.3234	0.0308	0.0002	0.5619	0.0836
ϕ_{11}	0.5394	0.1889	0.0158	0.2104	0.0456
ϕ_{21}	0.3551	0.1884	0.0212	0.3947	0.0407
ϕ_{12}	0.3696	0.1717	0.0238	0.3966	0.0384
ϕ_{22}	0.5249	0.1718	0.0191	0.2412	0.0429
φ_3	0.3434	0.0624	0.0160	0.5301	0.0480
φ_4	0.5861	0.1403	0.1786	0.0592	0.0357
ϕ_{PP}[a]	0.4858	0.1407	0.0284	0.3492	0.0358

[a] For comparison, the bottom line reports the distribution computed for a dihedral of isotactic polypropylene (ϕ_{PP}) according to Suter and Flory's statistics.[17]

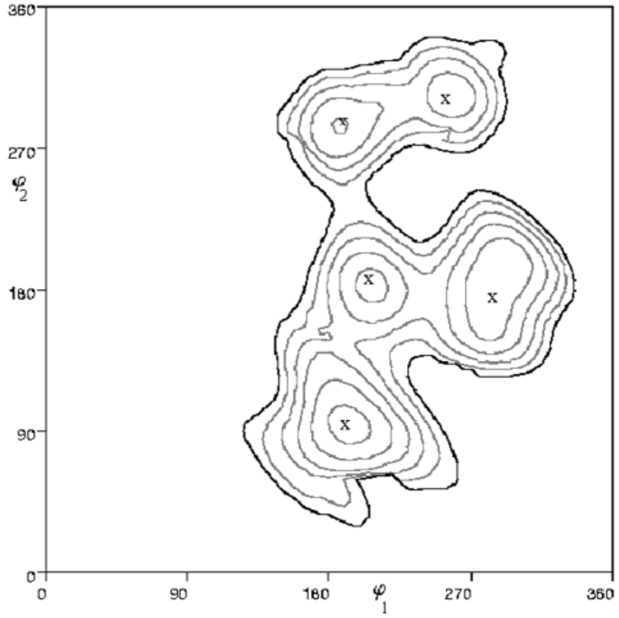

Figure 5. Energy map $E(\varphi_1,\varphi_2)$ of NPN for $c' = c'' = 2$ and state *t* of dihedral φ_0. Contours separated by an energy difference of 5 kJ/mol.

Table 4. Nonzero Statistical Weights $w_{NPN}(i_1,i_2,i_0;1,1)$ Obtained from MM2 Energy Maps of NPN at 100 °C[a]

	average conformation			states			w_{NPN} $(i_1,i_2,i_0;1,1)$
state *s*	$\langle\varphi_1\rangle$	$\langle\varphi_2\rangle$	$\langle\varphi_0\rangle$	i_1	i_2	i_0	MM2
1	−167	95	−161	1	3	1	0.3519
2	−75	−177	−162	4	1	1	0.2283
3	−155	178	−159	2	1	1	0.0560
4	−167	−74	−159	1	5	1	0.0376
5	−101	−56	−158	3	5	1	0.0157
6	−74	−174	−77	4	1	2	0.0614
7	−160	157	−78	1	2	2	0.0704
8	−174	60	61	1	4	3	0.1330
9	−93	159	64	3	1	3	0.0450

[a] Conformational states and average angles are referred to configuration *L*/*S*/*L*.

Discussion

Isotactic Copolymers with Mid−Low N Content. The above results on the RIS model of the P−N chain show significant discrepancies between the MM2 and

Table 5. Comparison among Relative Energies of Most Stable Conformers of PSLP (Stereoisomer of PPNP with $c = c' = c'' = 1$), Minimized with Molecular Mechanics (MM2 and MM3 with Solvent) and with ab Initio (B3LYP/6-31G) Methods**

	conformer	relative energies [kcal/mol]			dihedrals [deg][a]					population[b]	
item	($\varphi_3\varphi_4/\varphi_0/\varphi_1\varphi_2$)	MM2	MM3+solv	Ab initio[a]	φ_3	φ_4	φ_0	φ_1	φ_2	MM2	MM2corr
1	g′t/t/tg	0.	0.	0.	−59	−176	−159	−167	71	0.1174	0.1583
3	g′t/g′/tg	0.31	1.02	0.46	−59	176	−75	−162	72	0.1349	0.1486
7	tg+/t/tg	1.02	1.66	1.12	−165	93	−160	−169	70	0.1010	0.1208
4	g′t/t/t+t	1.24	1.84	1.29	−59	−176	−167	−142	175	0.0412	0.0522
d	g′t/g′/t+t	0.91	2.32	1.47	−60	175	−74	−146	175	0.0734	0.0414
2	g′t/g/tg	1.97	2.90	2.03	−59	173	68	−165	71	0.0128	0.0159
8	tg/g/tg	1.53	2.98	2.22	−177	50	64	−165	71	0.0472	0.0255
b	t+t/t/tg	2.31	2.61	2.22	−140	−180	−157	−167	71	0.0143	0.0221
6	g′t/g′/g′-t	1.74	2.97	2.39	−58	−178	−81	−84	168	0.0686	0.0386
a	tt-/g′/tg	1.81	3.40	2.41	−175	139	−75	−168	68	0.0329	0.0200
9	g′t/t/t+g′	2.00	2.86	2.44	−59	−176	−163	−148	−58	0.0154	0.0121
e	g′t/g′/t+g′	1.90	3.29	2.53	−59	175	−74	−146	−59	0.0235	0.0261
5	g′t/g/t+t	3.22	4.70	3.33	−59	173	66	−144	175	0.0008	0.0010
c	tg+/t/t+g′	3.12	4.57	3.69	−165	94	−162	−148	−58	0.0132	0.0093

[a] Minimum-energy geometry computed ab initio with B3LYP/6-31G**. [b] Conformer populations in the PSLP moiety in an isotactic $(N-P_4)_x$ copolymer, computed with MM2 and MM2corr statistics, respectively.

Table 6. Comparison between Relative Energies of Most Stable Conformers of *L/S/L* (Stereoisomer of NPN with $c' = c'' = 1$), Minimized with Molecular Mechanics (MM2 and MM3 with Solvent) and with ab Initio (B3LYP/6-31G) Methods**

	conformer	relative energies [kcal/mol]			dihedrals [deg][a]			populations[b]	
state *s*	($\varphi_1\varphi_2/\varphi_0$)	MM2	MM3+solv	ab initio[a]	φ_1	φ_2	φ_0	MM2	MM2corr
1	tg+/t	0.	0.	0.	−167	95	−160	0.168	0.359
2	g′t/t	0.80	0.24	0.28	−80	180	−163	0.109	0.135
3	t+t/t	1.32	1.03	0.68	−148	−177	−158	0.038	0.171
7	t+t/g′	1.62	2.15	1.37	−146	178	−76	0.487	0.175
8	tg/g	0.96	1.68	1.45	−178	52	63	0.152	0.072
9	g′t-/g	1.88	2.72	1.82	−80	149	62	0.023	0.025
6	g′t/g′	1.34	2.03	1.89	−74	−176	−77	0.016	0.041
4	tg′/t	1.62	1.96	2.23	−170	−75	−158	0.006	0.021
5	g′−g′/t	2.04	2.78	2.36	−101	−56	−158	0.001	0.001

[a] Minimum-energy geometry computed ab initio with B3LYP/6-31G**. [b] Conformer populations in a *L*/*S*/*L* unit of an isotactic alternating $(P-N)_x$ copolymer, computed with MM2 and MM2corr statistics, respectively.

Table 7. ^{13}C Chemical Shifts[a] for the Stable Conformers of PSLP (See Table 5) Computed with the Method MPW1PW91/6-311+G(2d,p)

item	1	3	7	4	d	2	8	b	6	a	9	e	c
conformer	g′tttg	g′tg′tg	tg+ttg	g′ttt+t	g′tg′t+t	g′tgtg	tg g tg	t+tt tg	g′tg′g′t	tt−g′tg	g′ttt+g′	g′tg′ t+g′	tg+tt+g′
carbon													
Pδ′ [b]	20.09	19.77	24.44	20.22	19.76	19.98	25.18	26.82	20.49	25.52	20.18	19.68	25.54
Pδ	25.32	25.50	21.32	25.25	25.54	25.18	20.84	25.32	25.47	21.75	25.30	25.48	21.23
Tγ	28.97	29.75	32.20	28.83	29.66	28.91	29.79	32.43	30.17	34.96	29.17	29.35	33.18
Sβ	45.64	43.15	47.75	46.02	43.03	47.71	47.93	44.38	44.10	42.05	45.86	43.20	47.80
Pβ	21.42	20.32	26.23	19.94	20.20	13.44	18.91	23.31	21.08	25.45	20.66	20.25	25.19
Tα	30.90	33.93	31.95	32.60	34.69	39.71	39.55	36.39	33.47	37.20	32.59	34.59	32.53
C2	57.72	57.23	59.46	58.80	57.44	57.18	49.66	57.75	56.67	57.63	58.59	58.22	60.36
C1	42.26	42.18	43.93	41.41	41.87	48.72	48.45	42.41	42.44	42.92	41.75	41.57	43.74
C7	35.82	38.00	36.30	36.22	38.18	37.38	37.89	35.45	38.11	38.31	35.87	37.69	36.12
C6	34.75	35.07	34.84	35.17	34.98	35.34	35.14	34.58	34.14	36.26	34.76	35.00	34.87
C5	32.24	32.77	32.43	31.16	32.30	32.20	32.33	32.35	34.00	32.76	31.52	32.11	32.00
C4	46.25	45.54	46.47	49.50	47.83	45.31	45.95	45.78	50.35	43.69	49.95	47.76	50.68
C3	47.60	50.18	47.89	50.67	52.73	51.17	51.21	47.45	49.42	50.04	43.90	46.40	43.55
Sα	40.57	41.88	40.57	40.19	41.91	43.24	43.26	40.88	43.11	40.58	37.76	39.30	37.51
Tβ	31.28	32.26	31.38	36.91	36.59	32.45	31.90	31.15	34.33	30.39	32.97	32.80	32.92
Pγ′ [b]	21.04	20.88	20.89	25.16	25.29	21.06	20.97	20.84	24.95	20.74	22.11	21.84	22.08
Pγ	25.43	25.50	25.54	22.09	22.13	25.70	25.58	25.55	21.09	25.68	21.40	21.29	21.37

[a] Referred to TMS, whose absolute value is computed as 186.96 ppm. [b] Pδ′ and Pγ′ represent the terminal methyls that become methylenes in the isotactic copolymer.

MM3 force fields. Indeed, although the order in the relative stability of the major conformers, shown in Table S1, is nearly the same, quantitative differences are found in the statistical weights *w*. Nevertheless, it appears possible to draw a number of unambiguous indications on the conformer populations, which may be of great help for the signal assignment of the ^{13}C NMR spectra of P−N copolymers. Moreover, the ab initio results are usually, at least for the most important conformers, in good agreement with MM2, and in all cases they are closer to this force field than to MM3. Therefore, we shall refer to the conformer populations calculated with MM2 and also with a third set of weights obtained from the MM2 maps but corrected for the minimum-energy differences between the MM2 and ab initio methods.

The P−N chain obviously turns out to be much more rigid than an E−N chain having the same N content. Owing to the strong interactions of Pβ (and less strong of Pγ) with the norbornene ring, the conformational

Table 8. ^{13}C Chemical Shifts[a] for the Stable Conformers of Compound 3 (Isomer *L/S/L*, See Table 6) Computed with the Method MPW1PW91/6-311+G(2d,p)

item	1	2	3	7	8	9	6	4
conformer	*tgt*	*g′tt+*	*ttt*	*ttg′*	*tgg*	*g′tg*	*g′tg′*	*tg′t*
carbon								
Pα	16.64	16.83	18.09	18.25	16.17	16.81	16.79	16.03
C2	44.90	44.77	46.87	46.52	45.37	44.42	44.40	45.44
C1	49.18	49.63	48.82	48.83	49.31	49.43	49.38	48.07
C7	34.80	35.75	35.30	35.35	34.86	35.23	35.22	34.89
C6	32.92	32.08	33.83	33.01	32.98	32.23	32.30	33.45
C5	33.29	33.72	33.10	32.56	32.98	33.65	33.61	32.40
C4	44.37	50.75	48.59	49.35	43.05	50.50	50.48	44.62
C3	50.88	45.21	49.88	50.61	47.25	48.22	48.13	43.34
Sαβ	38.83	40.15	36.21	34.26	38.18	41.70	41.73	33.64
Tαβ	33.99	34.22	39.91	40.25	40.93	42.74	42.68	34.63
Pβ	26.12	22.60	23.40	22.45	19.68	15.91	15.97	21.28
C2′	59.04	57.98	58.21	56.85	48.66	55.34	55.13	54.25
C1′	44.93	42.68	42.61	43.04	48.58	48.80	48.80	43.32
C7′	36.02	36.38	35.39	36.96	37.70	37.04	37.20	34.97
C6′	34.98	35.09	34.92	34.74	35.27	34.61	34.90	33.77
C5′	32.20	31.83	32.21	32.59	32.31	32.68	32.73	31.57
C4′	50.15	49.73	49.43	47.93	50.23	49.39	48.58	49.63
C3′	44.40	44.94	45.05	47.89	48.30	47.74	49.98	45.06
Pα′	16.72	16.75	16.46	17.28	19.47	19.69	19.67	16.32

[a] Referred to TMS, whose absolute value is computed as 186.96 ppm.

space accessible to dyad (φ_1, φ_2), and also to dyad (φ_3, φ_4), is greatly altered and reduced in comparison with a PP dyad. This is evidenced in Table 3 by the differences between the conformer distributions of the four dyads, which are also compared with the distribution computed for isotactic polypropylene according to Suter and Flory[17] (ϕ_{PP}). Moreover, the conformer distributions for the five φ dihedrals strongly depend on some if not all components of the configuration vector **c**. Detailed considerations on this point can be found in supplement SA of the Supporting Information.

Careful analysis of the dependence of the conformer populations for various dihedrals of the isotactic chain on the distance from the norbornene rings (see Table S4) showed that for the five φ dihedrals, on which the chemical shifts of the N carbons are expected to depend, the changes drop to negligible values (<0.02) for $n > 2$. Also for dihedrals (ϕ_{1i}, ϕ_{2i}) of the PP dyads the changes are similarly small for $i > 2$ and $n - i > 2$. Therefore, it seems reasonable, at this first approach to the interpretation of P−N NMR spectra, to rely on populations computed for $n = 2$ for estimating conformational effects on the chemical shifts in copolymers with low N content. The last two columns of Table 5 show the conformer populations of the PPNP moiety of the isotactic chain $(N-P_4)_x$, calculated with the MM2 and MM2corr statistics, respectively. These populations are the basis for averaging the theoretical chemical shifts. It should be noted that such distributions do not strictly reflect the relative energies of the PPNP conformers, owing to the correlation with the rest of the chain. It should be pointed out that such 5-dihedral probabilities are used to predict the chemical shifts, rather than the populations of Table 3 that are functions of a single dihedral, since for norbornene carbons we cannot rely on established empirical relationships between conformation and chemical shifts, as occurred in the past, for example, in the analysis of PP ^{13}C spectra.[9] The two sets of populations of Table 5 present discrepancies of only a few percent, thus offering quite clear indications in view of chemical shift averaging for P−N copolymers with low N content.

Isotactic Alternating Copolymer. More uncertain appears the possibility of predicting conformational effects in copolymers having high N content, e.g., in alternating copolymers. Table 4 shows that only nine conformers (defined by dihedrals φ_1, φ_2, and φ_0) participate to the equilibrium of compound NPN representing the basic fragment of the isotactic alternating copolymer. This apparently simple situation is complicated by the fact that in compound **4** the nine states combine in a rather unpredictable fashion, so that some states with low w_{NPN} values become important when applying eq 9 to compute the average copolymer conformation. Further details on the strong interactions between adjacent NPN units are provided in supplement SB. The results of the ab initio computations on the nine conformers of **3** and on a dozen of the most stable states of **4** present discrepancies with respect to the MM2 results that are not much greater than those seen previously but have greater effects on the conformer populations, owing to the strong correlation. Comparison between the two last columns of Table 6 shows that the effects of the quantum-mechanical corrections on the populations are dramatic; considering the populations at the single dihedrals, the differences concern φ_0 above all. At the moment, we may conclude that the average conformation of the isotactic alternating P−N copolymer mainly involves a few conformational states represented in the upper part of Table 6, while further work is needed to clarify the behavior of this highly strain polymer chain.

Comparison of Average ^{13}C Chemical Shifts with Experiment. Here we shall only summarize the detailed analysis of P−N copolymer ^{13}C NMR spectra reported in paper 2.[15] These spectra appear quite complex, their numerous signals spanning a wide range of chemical shifts from 15 to 55 ppm. Comparison with the spectra of polypropylene and E−N copolymers and DEPT experiments led us to a first preliminary assignment (see Table 2 of paper 2), which distinguishes three bands associated with the propene carbons and identifies seven major signals as arising from the four different types of norbornene carbons. Then we resorted to the ab initio chemical shifts averaged over the RIS populations in order to confirm and extend such assignments. The basic assumption underlying our procedure is that, although the absolute ab initio shieldings may

Table 9. Chemical Shifts (ppm) Expected and Observed for Some Carbons of Isotactic P−N Copolymers

atom	exptl[7c] (E−N cop)	calcd (DPN)	correction	average (MM2)	average (MM2corr)	expected (MM2corr)	obsd[15]
C2	45.03	51.37	1.0/1.5	57.50	57.82	52.7	53.33
C1	39.50	45.13	−0.5	43.18	43.13	37.0	37.28
C7	30.90	35.81		37.13	36.89	31.98	31.91
C6	28.33	33.47		34.94	34.93	29.79	30.10
C5	28.33	33.47		32.47	32.38	27.24	27.34
C4	39.50	45.13	−0.5	47.16	46.93	40.8	41.54
C3	45.03	51.37	1.0/1.5	49.45	49.17	44.1	45.61
Pβ	19.69[a]	20.67[b]	−0.1/−0.2	21.99	22.02	20.9	21.24

[a] The reference experimental chemical shift for carbon Pβ is the methyl signal of the *mmmm* PP pentad.[25] [b] Chemical shift computed for central methyl of the (*tgtg*) conformer of 2,4,6-trimethylheptane.

be affected by errors on the order of 5 ppm, the observed chemical shift differences between carbons that are chemically equivalent but differ in their conformational/geometrical environments are well reproduced by the calculated differences.[12] Hence, the expected value of the chemical shift of a given carbon of our copolymer is derived from the known experimental signal of that carbon in a well-assigned reference copolymer and from the differences between the chemical shifts computed for the model compounds of the two copolymers. For the seven norbornene carbons, the reference chemical shifts are the signals observed for the isolated N ring of a sequence E−E−N−E−E in the spectra of E−N copolymers, and we take the *all-anti* conformer of 2,3-di-*n*-propylnorbornane (DPN) as model compound of the isolated N of an E−N copolymer. Thus, we calculate

$$\nu_{\text{expect}} = \nu_{\text{exptl}}(\text{E}-\text{N cop}) + \nu_{\text{average}} - \nu_{\text{calcd}}(\text{DPN})\ (+\ \text{correction}) \quad (10)$$

where the correction term in some cases accounts for deficiencies of the isolated N model. The results are summarized in Table 9. The fifth and sixth columns report the average chemical shifts computed for the N carbons of the isotactic $(\text{P}_4-\text{N})_x$ chain on the basis of the ab initio values of Table 7 and the conformer populations given in Table 5 according to the MM2 and MM2corr statistics, respectively. This averaging was done by extending the sample of 13 conformers (representing 69% of the whole population) to other conformers (from 82 to 100%) on the basis of the observation that chemical shifts are functions of only some of the five PPNP torsional angles (see paper 2 for more details). Different averaging and different statistics (purely MM or QM corrected) indicate discrepancies never greater than 0.3 ppm. Somewhat greater uncertainty affects the correction term applied to the chemical shifts of carbons C2/C3 (and to a lesser extent of C1/C4). Such corrections, which do not affect the differences between two chemically equivalent carbons, are due to the fact that the *all-anti* conformer of model compound DPN does not exactly represent the situation of the isolated norbornene of E−N copolymers, where *gauche* conformations have significant probabilities. Such uncertainties are anyway quite small compared with the splittings displayed by the expected values of the three pairs C5/C6, C2/C3, and C1/C4. Hence, if the clear indications of these calculations are adopted to assign the seven distinct major observed N signals, comparison of the last two columns of Table 9 shows that the three CH_2 chemical shifts are reproduced accurately and that also the values for the four CH carbons, most severely perturbed from the symmetrical condition of the isolated N, are in reasonable agreement. We should add that, if one utilizes the data of Tables 6 and 8 to calculate the average chemical shifts of the alternating $(\text{P}-\text{N})_x$ copolymer, the discrepancies found between the values obtained with the two statistics are surprisingly small (except for C2, 1.1 ppm), notwithstanding the large differences displayed by the conformer populations, and the expected values differ by 0.5−1.2 ppm from those given in Table 9 for the seven N carbons, thus suggesting the origin of the rather large signal bands observed in the spectra of high N content copolymers.

The bottom line of Table 9 shows the chemical shift expected for methyl Pβ, estimated by means of eq 10 by taking the central methyl of 2,4,6-trimethylheptane (TMH) as a model of isotactic polypropylene methyl. The result suggests the assignment to Pβ of the major propene signal observed at 21.2 ppm.

Conclusions

A RIS description of the chain of propene−norbornene copolymers has been achieved by means of molecular mechanics. The conformational model was checked and corrected on the basis of ab initio computations. Quantum-mechanical methods (GIAO/DFT) were then utilized for computing the ^{13}C chemical shifts of P−N model compounds. The theoretical chemical shifts, averaged over the RIS populations of a chain representing P−N copolymers with mid−low norbornene content and compared with the chemical shifts computed for a model compound of the isolated N unit of an E−N copolymer, yield expected values for the seven N carbons in good agreement with the major observed signals independently assigned to norbornene carbons. Thus, the calculations quantitatively clarify the splittings of the signals of C5/C6, C1/C4, and C2/C3 carbon pairs and allow for a first unambiguous assignment of each of the seven major N signals. This is a basic step toward the understanding of the microstructure of P−N copolymers.

In conclusion, accurate quantum-mechanical computations of ^{13}C chemical shifts perfomed on relevant conformers of proper model compounds, combined with other computational techniques for assessing the conformer populations, appear to be a powerful tool to help the elucidation of polymer microstructure from their ^{13}C NMR spectra. This methodology may be particularly useful for those macromolecular systems where empirical relationships between conformation and chemical shifts are not available.

Acknowledgment. Financial support from the Italian “Ministero dell’Università e della Ricerca Scientifica e Tecnologica” (Project FISR-2000) is gratefully acknowledged.

Supporting Information Available: Most stable minimum-energy conformers of PNP (Table S1); nonzero statistical weights $w_{\mathrm{PPN}}(i_3,i_4,i_0;1,2)$ (Table S2); conformer distributions for the φ dihedrals of a $(\mathrm{N}-\mathrm{P}_4)_x$ chain for different configurations **c** (Table S3); conformer distributions for nine dihedral angles of an isotactic chain $(\mathrm{N}-\mathrm{P}_{n+2})_x$ for various values of n (Table S4); relative energies of 9 × 9 conformers of compound **4** (Table S5); relative MM2 and ab initio energies selected conformers of isomer $L/S/L/S/L$ of compound **4** (Table S5); dependence of conformer distribution on configuration **c** (Supplement SA); and correlation between NPN fragments in the alternating $(\mathrm{P}-\mathrm{N})_x$ chain (Supplement SB). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kaminsky, W.; Bark, A.; Arndt, M. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 83.

(2) (a) Arndt, M.; Engehausen, R.; Kaminsky, W.; Zoumis, K. *J. Mol. Catal., A: Chem.* **1995**, *101*, 171. (b) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221. (c) Arndt-Rosenau, M.; Beulich, I. *Macromolecules* **1999**, *32*, 7335.

(3) (a) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4674. (b) Wendt, R. A.; Mynott, R.; Hauschild, K.; Ruchatz, D.; Fink, G. *Macromol. Chem. Phys.* **1999**, *200*, 1340.

(4) Bergström, C. H.; Sperlich, B. R.; Ruotoistenmäki, J.; Seppälä, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1633.

(5) Harrington, B. A.; Crowther, D. J. *J. Mol. Catal., A: Chem.* **1998**, *128*, 79.

(6) McNight, A. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 42816.

(7) (a) Tritto, I.; Boggioni, L.; Sacchi, M. C.; Locatelli, P.; Ferro, D. R.; Provasoli, A. In *Metalorganic Catalysis for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer: Berlin, 1999; p 493. (b) Provasoli, A.; Ferro, D. R.; Tritto, I.; Boggioni, L. *Macromolecules* **1999**, *32*, 6697. (c) Tritto, I.; Marestin, C.; Boggioni, L.; Zetta, L.; Provasoli, A.; Ferro, D. R. *Macromolecules* **2000**, *33*, 8931. (d) Tritto, I.; Marestin, C.; Boggioni, L.; Sacchi, M. C.; Brintzinger, H.-H.; Ferro, D. R. *Macromolecules* **2001**, *34*, 5770.

(8) (a) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612. (b) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 5318.

(9) (a) Provasoli, A.; Ferro, D. R. *Macromolecules* **1977**, *10*, 874. (b) Ferro, D. R.; Ragazzi, M. *Macromolecules* **1984**, *17*, 485.

(10) Chesnut, D. B. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, Chapter 5.

(11) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hinton, J. F.; Pulay, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(12) Ragazzi, M.; Carbone, P.; Ferro, D. R. *Int. J. Quantum Chem.* **2002**, *88*, 663.

(13) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(14) Hensche, O.; Köller, F. *Macromol. Rapid Commun.* **1997**, *18*, 617.

(15) Boggioni, L.; Bertini, F.; Zannoni, G.; Tritto, I.; Carbone, P.; Ragazzi, M.; Ferro, D. R. *Macromolecules* **2003**, *36*, xxxx.

(16) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969; Chapter 1.

(17) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.

(18) (a) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *12*, 395. (b) Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8552.

(19) *MacroModel*, version 5.5; Department of Chemistry, Columbia University, New York, 1996.

(20) Ferro, D. R.; Ragazzi, M. *Molecular Mechanics Program CHAMP*; ICM-CNR: Milano, Italy, 1993.

(21) Wiberg, K. B. *J. Comput. Chem.* **1999**, *20*, 1299.

(22) *Jaguar 3.5*; Schroedinger, Inc., Portland, OR, 1998.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Jameson, A. K.; Jameson, C. J. *Chem. Phys. Lett.* **1987**, *134*, 461.

(25) Carvill, A.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromolecules* **1997**, *30*, 7056.

MA021247E