Propene−Norbornene Copolymers: Synthesis and Analysis of Polymer Structure by ^{13}C NMR Spectroscopy and ab Initio Chemical Shift Computations

Laura Boggioni, Fabio Bertini, Giulio Zannoni, Incoronata Tritto,*
Paola Carbone, Massimo Ragazzi, 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 series of propene−norbornene (P−N) copolymers were synthesized in the presence of *rac*-Et(indeny)$_2$ZrCl$_2$/MAO in toluene at 30 °C. P−N copolymers were characterized by ^{13}C NMR spectroscopy, SEC, and DSC. Results were compared with those of a series of P−N copolymers synthesized in the presence of *rac*-Me$_2$Si(Indenyl)$_2$ZrCl$_2$/MAO under the same experimental conditions. Polymerization activity appears to be quite low in comparison with ethene−norbornene (E−N) copolymerization. A first assignment of the main ^{13}C NMR signals of P−N copolymers containing isolated N units was obtained on the basis of distortionless enhancement by polarization transfer (DEPT) ^{13}C spectra and by comparison with isotactic polypropene (*i*-PP) and E−N copolymer spectra. Ab initio theoretical ^{13}C NMR chemical shifts, computed for the most relevant conformers of a rather simple model compound and averaged using the RIS conformer populations estimated for an isotactic chain $(P_4−N)_x$, gave important detailed indications for the assignment of the complex ^{13}C spectra of P−N copolymers with N content up to 35 mol %. Such assignments were used to estimate the N copolymer content. The discrepancy between the values obtained from the areas of methyl signals and from the areas of the signals assigned to norbornene carbons was found to be partially due to the presence of 1,3-propene misinsertions, which are formed in significant amount when increasing the [N]/[P] ratio of the feed. Our results confirm that, despite the relatively lower polymerization activity, at low norbornene/olefin ratio it is possible to obtain P−N copolymers that are relatively richer in norbornene than the E−N copolymers prepared in similar conditions. However, at higher norbornene/olefin feed ratios the great amount of 1,3-propene misinsertions clearly reveals that the steric hindrance of the Mt−tertiary carbon bond when N is the last inserted unit makes difficult the next propene insertion, causing low polymerization activities, molecular masses, and T_g.

Introduction

Metallocene-based catalysts offer opportunities for the synthesis of olefin−cycloolefin copolymers (COC). These products, usually amorphous and thermoplastic, form a new class of materials endowed with such properties as excellent transparency, good heat resistance, and high glass transition temperature.[1] The properties of ethene−norbornene (E−N) copolymers can be easily modulated by varying and controlling their composition and microstructure; e.g., their glass transition temperature (T_g) can reach values higher than 220 °C. The incorporation of norbornene into the isotactic polypropene chain was expected to greatly affect polymer properties; since polypropene (PP) has a higher T_g than polyethene, P−N copolymers were expected to feature higher T_g than E−N copolymers with the same N content and molar mass (MM). Nevertheless, to the best of our knowledge, only one article concerning propene−norbornene (P−N) copolymers has been published,[2] besides short references to propene-based co- and terpolymers.[3] P−N copolymers with a norbornene content up to 98 mol % were claimed to result using *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$ with methylaluminoxane (MAO).[2] Copolymer composition was reported[2] to be determined from a comparison of the intensities of the methyl carbons (or protons) with the total intensities of NMR signals, without any spectroscopic detail.

Our group has devoted considerable effort to the synthesis and the study of the microstructure of E−N copolymers by ^{13}C NMR analysis.[4] It is foreseen that a detailed interpretation of P−N copolymer spectra will meet greater difficulties compared with those of E−N copolymers, owing to the complexity of stereo- and regioregularity of the propene units as well as to that of the comonomer distribution and of the stereoregularity of the bicyclic units. These difficulties may have limited the studies on P−N copolymers so far. Given the great general interest in norbornene copolymers, we have undertaken a study of P−N copolymerization with specific regard to the elucidation of their structure.

As shown by our previous work on E−N copolymers, assignment of the ^{13}C signals may be made easier by the elucidation of the chain conformation and by relationships between conformation and chemical shifts.[4b] More recently, we found that a precious help can come from ab initio quanto-mechanical (DFT/GIAO) chemical shift computations.[5] Therefore, to clarify the microstructure of P−N copolymers, a conformational (RIS) model of the P−N chain was worked out, and the chemical shifts of stable conformers of proper model compounds were computed ab initio. Details of those computations are presented in the adjoining article, which we shall refer to as paper 1.[6] Here we present the synthesis of a series of P−N copolymers by using *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**) with methylaluminoxane (MAO) along with their ^{13}C NMR spectra and the assignments of the spectra. The computed conformer populations presented in paper 1 will be combined with the theoretical chemical shift differences in order to achieve a first significant interpretation of the P−N copolymer spectra. Moreover, a

---

* Corresponding author: e-mail i.tritto@ismac.cnr.it.

10.1021/ma0212487 CCC: $25.00

Table 1. Comparison of P−N and E−N[a] Copolymerizations

catalyst	*T* (°C)	[N]/[P]	activity[b]	mol % N in the copolymer	*T* (°C)	[N]/[E]	mol % N in the copolymer[e]
1	30	0.10	70	23[c]	30	0.11	4.0
1	30	0.26	56	35[c]	30	0.25	8.5
1	30	1.00	9	41[c]	30	1.00	22.5
2	60	0.11	320[2]	11[d]	60	0.11	5.0
2	60	0.33	140[2]	33[d]	60	0.32	15.0
2	60	1.00	60[2]	56[d]	60	1.00	23.0

[a] Polymerization conditions: toluene = 100 mL, [Al]/[Zr] = 2000, $T = 30$ °C, [Zr] = 20×10^{-6} mol/L, $t = 1$ h, $p_{C3} = 1.01$ atm. [b] Activity = polymer kg/Zr mol h. [c] See Table 5 and section Calculation of N content. [d] The authors[2] declare to have derived the N content from the polypropylene methyl intensities of ^{1}H and ^{13}C NMR spectra. [e] Unpublished data of our laboratory.

series of P−N copolymers have been synthesized in the presence of *rac*-$Me_2Si(indenyl)_2ZrCl_2$/MAO (**2**)/MAO for comparison.

Results and Discussion

Synthesis and Preliminary Assignments of the ^{13}C NMR Spectra. Catalyst **1** was selected as an *ansa*-metallocene of C_2 symmetry that has proven effective for producing prevailingly isotactic and regioregular polypropene[7] as well as E−N copolymers[1a] with a tendency to alternate ($r_1r_2 = 0.072$).[8] Copolymerizations of propene and norbornene were carried out with catalyst **1**/MAO in toluene over a wide range of molar feed ratios at 30 °C, an [Al]/[Zr] molar ratio of 2000, to allow comparison with the results obtained for E−N copolymerization. Polymerization tests have been designed to ensure low comonomer conversion and also to yield enough copolymer to be studied by NMR and DSC. Copolymerization data are reported in Table 1, where we compare selected results of P−N polymerization activity with catalyst **1** and literature data[2] obtained by using the catalytic system **2**/MAO. For sake of comparison, results of E−N copolymerizations with the same catalysts are also reported. The data show that as the feed ratio ([N]/[P]) increases the productivity decreases, as expected. This agrees with the results obtained using *rac*-$Me_2Si(indenyl)_2ZrCl_2$ and is analogous to those of the E−N copolymerization.

The polymerization activities are quite low, especially when compared to those obtained for E−N copolymerization under analogous experimental conditions.[1,4] Such a result may reflect the difficulty of inserting a propene in a Mt−N bond, that is, in a Mt−tertiary carbon bond. Indeed, such a situation is even more sterically crowded than the sites formed after a propene (2,1) regioirregular insertion, which have a lower reactivity with respect to sites with a primary growing polypropene chain.[9]

In contrast to the low polymerization activity, a surprisingly high norbornene incorporation was reported[2] using *rac*-$Me_2Si(indenyl)_2ZrCl_2$, although to date no NMR spectra or details of such calculations are published.

The structure and carbon numbering of an isotactic poly(P-*co*-N) are sketched in Figure 1. On the basis of previous studies, 2,3 norbornene insertion is considered to occur into the metal−carbon bond, the *exo* face being more reactive than the *endo* face. The two propene consecutive monomer units have the methyls in erythro relationships as in an isotactic polypropene chain.

The ^{13}C NMR spectra of two P−N copolymers with different norbornene contents are displayed in Figure 2. It is apparent that signals of the spectra of all copolymer samples span a wide range of chemical shifts from about 15 to about 55 ppm. Spectra of copolymer samples prepared at high norbornene concentration are quite complex.

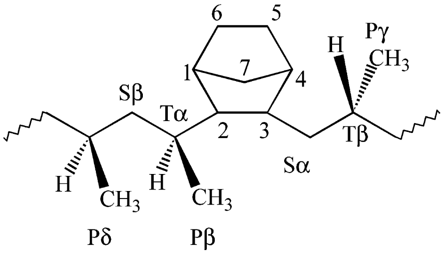

Figure 1. Structure and carbon numbering of an isotactic poly(P-*co*-N). P, S, and T denote primary, secondary, and tertiary propene carbons, respectively. Greek letters denote the distance of a given carbon from the closest tertiary norbornene carbon.

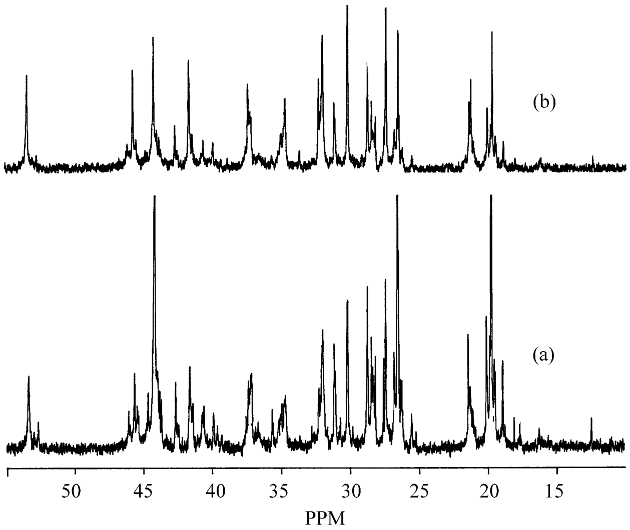

Figure 2. ^{13}C NMR spectra of P−N copolymers prepared at [N]/[P] feed ratio 0.05 (a) and 0.07 (b) in the presence of **1**/MAO. Chemical shifts are referred to HMDS: δ(HMDS) ≈ δ(TMS) −2.0 ppm.

A first general assignment, reported in Table 2, is based on distortionless enhancement by polarization transfer (DEPT) ^{13}C spectra (Figure 3) and on comparison with PP and E−N copolymer spectra. DEPT experiments where the intensities of signals depend on the θ pulse of the sequence applied allow one to distinguish signals of methyl, methine, and methylene carbons. In the spectrum of Figure 3 the methine and methyl carbons appear positive, while the methylene ones are negative. Signals denoted T_{PP}, S_{PP}, and P_{PP} arise from tertiary, secondary, and primary carbons, respectively. They have chemical shifts very close to the corresponding carbons of polypropene; hence, we assign these groups of signals to methine, methylene, and methyl

Table 2. Comparison between ^{13}C Chemical Shifts of Propene Units in Isotactic PP[7] and P–N Copolymer and between ^{13}C Chemical Shifts of Norbornene Units in P–N and E–N[4] Copolymer

Propene

	chemical shifts (ppm)	
carbon	P–N	PP
CH_3 **(P)** *(mmmm)*	18.43–20.43 *(19.69)*	18.89–21.69 (*19.67*)
CH **(T)** *(mmmm)*	26.10–26.80 *(26.56)*	26.26–26.82 (*26.40*)
CH_2 **(S)** *(mmmm)*	43.64–44.69 *(44.19)*	43.81–44.70 (*44.10*)

Norbornene

	chemical shifts (ppm)	
carbon	P–N	E–N
C5/C6	27.33	28.33
C5/C6	30.09	28.33
C7	31.90	30.90
C1/C4	37.17	39.50
C1/C4	41.32	39.50
C2/C3	45.40	45.03
C2/C3	53.32	45.03

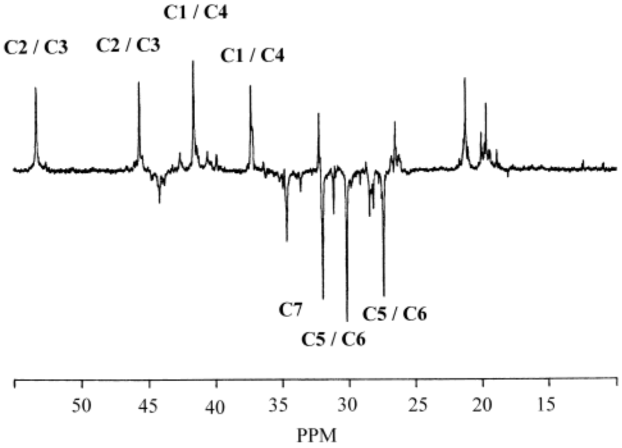

Figure 3. ^{13}C DEPT NMR spectrum (recorded at 103 °C in 1,1,2,2-tetrachloroethane-d_2) of a P–N copolymer prepared at [N]/[P] feed ratio 0.26 in the presence of **1**/MAO. Carbon numbering according to Figure 1.

carbons of propene units in polypropene blocks (Table 2).

The spectrum in Figure 3 shows four tertiary and three secondary signals with comparable areas, which should be due to the norbornene carbons. The number of signals indicates that there is no symmetry in the norbornene unit in agreement with the general structure depicted in Figure 1. The signals at 31.90, 30.09, and 27.33 ppm are secondary carbons and have to be assigned to C7 and C5/C6 norbornene carbons. The comparison of the chemical shifts of these signals with those of E–N copolymers may allow us to make a further step in assignments. The CH_2 signal at 31.90 ppm, being close to the signal of C7 of E–N copolymers (Table 2), can be reasonably assigned to C7. Therefore, the other two CH_2 signals pertain to carbons C5/C6. Indeed, they fall respectively to low and high field with respect to the C5/C6 signal of an isolated N unit in an E–N copolymer. The signals at 53.32, 45.40, 41.32, and 37.17 ppm are tertiary carbons and thus can be due to C2/C3 and C1/C4 carbons. By analogy with the E–N copolymers, the two major peaks on the left of the spectrum (45.40 and 53.32 ppm) should be assigned to C2/C3, while the remaining two peaks at 37.17 and 41.32 ppm should be assigned to carbons C1/C4.

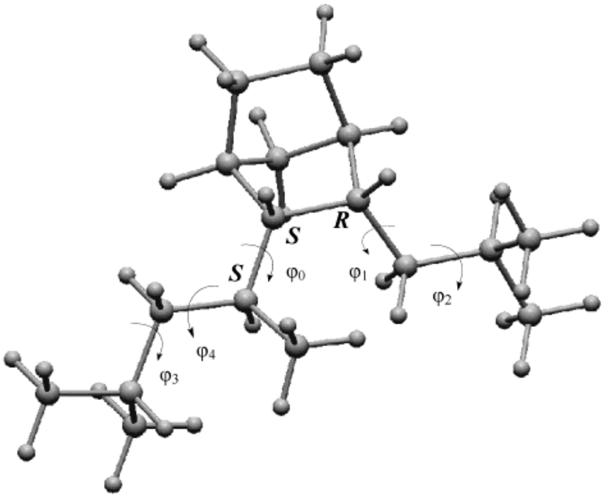

Figure 4. Model compound PSLP representing a segment of an isotactic poly(P-*co*-N) where the five main chain dihedral angles φ are shown.

Conformational Model and Theoretical Chemical Shifts. As we have mentioned, the conformational characteristics of an ideal P–N chain were investigated by means of molecular mechanics calculations. A rotational-isomeric-state model based on Allinger's force fields was worked out and verified and corrected with ab initio computations.[6] In this section, the major results of such calculations, namely the RIS populations estimated for an isotactic chain $(P_4{-}N)_x$ and the theoretical ^{13}C NMR chemical shifts computed for the most relevant conformers of model compound PSLP (shown in Figure 4), will be utilized to gain indications for the assignment of the complex ^{13}C spectra of mid-low N-content copolymers.

The conformations and the relative energies of the most stable conformers of PSLP, computed with the quantum-mechanical method B3LYP/6-31G**, are reported in Table 5 of paper 1.[6] The table also shows the relative energies obtained via molecular mechanics with force fields MM2 and MM3 and the conformer populations computed for the PSLP moiety of the isotactic $(P_4{-}N)_x$ copolymer, using the RIS statistics of the chain based on MM2 and the statistics corrected for the deviations from the ab initio computations (last two columns of the table, respectively). Thirteen of the PSLP conformers of Table 5 of paper 1 were utilized to compute their ^{13}C NMR chemical shifts with the ab initio method (GIAO/DFT) indicated as MPW1PW91/6-311+G(2d,p). Such theoretical chemical shifts are reported in Table 7 of paper 1. Here, in Table 3 we present the same results, for the norbornene carbons, in terms of differences with respect to the chemical shifts computed with the same method for the *all-trans* conformer of 2,3-di-*n*-propylnorbornane, which we take as a model for the isolated N unit of an E–N copolymer. As we do not rely on the absolute theoretical chemical shift values, such differences are of utmost importance for applying the present results to the interpretation of the ^{13}C NMR spectra of P–N copolymers. The 13 conformers of Table 3 account for 69% of the whole population (using the MM2corr statistics) of PSLP, which includes 81 conformers with nonzero probability, of which 22 have probability greater than 1%.

Table 4 shows the weight-averaged chemical shifts of the N carbons computed on the basis of the theoretical values of Table 7 of paper 1 and of the MM2 and

Table 3. ^{13}C Chemical Shifts of the Stable Conformers of PSLP Computed with Method MPW1PW91/6-311+G(2d,p), Expressed Relative to Model Compounds DPN (for N Carbons) and to TMH (for Carbon Pβ)

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*	*tggtg*	*t+tttg*	*g′tg′g′t*	*tt-g′tg*	*g′ttt+g′*	*g′tg′t+g′*	*tg+tt+g′*
P[a]		0.1583	0.1486	0.1208	0.0522	0.0414	0.0159	0.0255	0.0221	0.0386	0.0200	0.0121	0.0261	0.0093
carbon	DPN[b]													
C2	51.37	6.35	5.86	8.09	7.44	6.07	5.81	−1.71	6.38	5.30	6.26	7.22	6.85	8.99
C1	45.13	−2.87	−2.95	−1.20	−3.72	−3.24	3.59	3.31	−2.73	−2.68	−2.21	−3.38	−3.56	−1.39
C7	35.81	0.01	2.19	0.49	0.41	2.37	1.58	2.08	−0.35	2.30	2.50	0.06	1.88	0.31
C6	33.47	1.28	1.60	1.37	1.70	1.51	1.87	1.67	1.11	0.67	2.79	1.29	1.53	1.40
C5	33.47	−1.23	−0.70	−1.04	−2.31	−1.17	−1.27	−1.14	−1.12	0.53	−0.72	−1.95	−1.36	−1.47
C4	45.13	1.12	0.41	1.34	4.37	2.70	0.18	0.82	0.65	5.22	−1.44	4.82	2.63	5.55
C3	51.37	−3.77	−1.19	−3.48	−0.69	1.36	−0.20	−0.16	−3.91	−1.95	−1.32	−7.47	−4.96	−7.82
Pβ	20.67[c]	0.72	−0.35	5.56	−0.73	−0.47	−7.23	−1.76	2.64	0.41	4.78	−0.01	−0.42	4.52

[a] RIS populations computed for the PSLP moiety of the isotactic $(P_4-N)_x$ copolymer, using statistics MM2$_{corr}$ (see paper 1). [b] ^{13}C chemical shifts for the *all-trans* conformer of 2,3-di-*n*-propylnorbornane (DPN), computed with the same method and referred to TMS. [c] ^{13}C chemical shift of the central methyl of the *(tgtg)* conformer of 2,4,6-trimethylheptane (TMH).

Table 4. Chemical Shifts (ppm) Expected for Some Carbons of Isotactic P−N Copolymers on the Basis of ab Initio Differences between Corrected MM2 Statistical Averages and Reference Model Values (See Eq 1)

atom	av (MM2)	av (MM2corr)	expected (MM2corr)	obsd
C2	57.50	57.82	52.5/53.0	53.33
C1	43.18	43.13	37.1	37.28
C7	37.13	36.89	31.98	31.91
C6	34.94	34.93	29.79	30.10
C5	32.47	32.38	27.24	27.34
C4	47.16	46.93	40.8	41.54
C3	49.45	49.17	43.8/44.3	45.61
Pβ	21.99	22.02	20.9	21.24

MM2corr populations, respectively. Inspection of Tables 5 and 7 of paper 1 shows that the chemical shifts of a given carbon can be assumed to depend mainly on some of the five dihedrals that define the conformation of the PSLP moiety. This assumption allows one to extend the chemical shift averaging to a conformer population larger than the 69% of the available sample. For example, it was assumed that the chemical shifts of carbons C5/C6 depend only on dihedrals φ_0 and φ_1 (see Figure 4); hence, all PSLP conformers showing given values of the (φ_0, φ_1) pair were assigned the (weight-averaged) chemical shift value of these carbons computed for that (φ_0, φ_1) conformation. Thus, the averages of Table 4 refer to samples covering from 82 to 100% of the PSLP population. We notice that such estimates of the chemical shifts differ by not more than 0.3 ppm from the chemical shifts averaged over the 69% sample. We also note that discrepancies of the order of 0.3 ppm are found between the two sets of chemical shifts obtained with different statistics. The third column of Table 4 shows the expected chemical shift values, obtained by shifting the MM2corr average by the difference between the chemical shift observed in an isolated E−N copolymer and the value computed for di-*n*-propylnorbornane, in some cases with a correction described in the text:

$$\nu_{\text{expect}} = \nu_{\text{average}} + \nu_{\text{exptl}}(\text{E}-\text{N cop}) - \nu_{\text{calc}}(\text{di-}n\text{-propyl}-\text{N})\ (+\ \text{correction}) \quad (1)$$

In the following we discuss the results obtained for the different types of carbons.

Carbons C5/C6. The chemical shifts of these carbons are not affected by γ-*gauche*-type interactions with the chain. Hence, in alternating and isolated ENE sequences of E−N copolymers the unperturbed norbornene ring yields a unique signal. On the other hand, in the presence of ENNE sequences the strong inter-ring interactions cause a significant deformation of the ring that leads to distinct signals for “internal” (C6) and “external” (C5) carbons. It was found experimentally[4a,10,11] that the signals of external carbons are always shifted to low field with respect to the isolated C5/C6 signal and the internal ones to high field and that the size of the splitting and of the deformation depends on the *meso*/*racemic* relationship between the two N units.[4b] It has also been shown that the ab initio method used here is able to reproduce such splittings rather well.[5] As was expected, the methyl substitution in position α produces interactions around bond Tα−C2 similar to those at bond C2−C2′ of an NN diad. As a consequence, the chemical shifts computed for carbons C6 and C5 of the most stable conformer, *g′tttg*, are shifted by +1.28 and −1.23 ppm, respectively, with respect to the value computed for C5/C6 of the isolated model. Table 3 shows that similar splittings are computed also for most of the other conformers, so that the weight-averaged ab initio chemical shifts of C6 and C5 turn out to be shifted by +1.5 and −1.0 ppm with respect to the isolated model, respectively. This result fully justifies the assignment to C6 and C5 of the two major CH$_2$ signals found in the P−N spectra at 30.10 and 27.34 ppm, shifted by +1.8 and −1.0 ppm, respectively, with respect to the C5/C6 isolated signal of E−N at 28.33 ppm (see Table 4).

Carbon C7. The chemical shift of C7 computed ab initio for the most stable conformer coincides with the value of the isolated model (di-*n*-propylnorbornane); small relative shifts are found also for other conformers with dihedral φ_0 in the *t* state. On the other hand, shifts of 2−2.5 ppm are computed for conformers in the *g′* and *g* states of φ_0. Thus, the estimate based on the populations of these states yields an average shift of 1.08 ppm with respect to the isolated model. This result agrees very well with the assignment to carbon C7 of the major CH$_2$ signal observed at 31.91 ppm, shifted by +1.0 ppm from the C7 isolated signal of the E−N spectra.

Carbons C1/C4. If we simply extend to this pair of carbons the analogy, already found for C6/C5 between the effects of the asymmetry generated in a norbornene ring *N* by EN*N*E and by P*N*P (meaning $-CH_2-CH(CH_3)-N-CH_2-CH(CH_3)-$) sequences, which splits each signal of an isolated *N* into distinct signals for “internal” and “external” carbons, then for the bridgehead carbons of N in the P−N spectra we can qualitatively expect two signals, the one belonging to C1 lying at higher field. The spectrum presents two major CH signals at 37.28 and 41.54 ppm, shifted by −2.2 and +2.0 ppm from the C1/C4 isolated E−N signal, respectively. Thus, the signal splitting here is much greater than in the cases of *meso* and of *racemic* NN diads.

Indeed, a first inspection of Table 3 shows a difference of −3.99 ppm between the chemical shifts of C1 and C4 computed for the most stable conformer *g′tttg*, the former being shifted by −2.9 ppm and the latter by +1.1 with respect to the isolated model. The above hypothesis and assignment are so nicely confirmed. A detailed analysis of the results obtained for the other conformers moves the average chemical shifts of both carbons to low field, yielding differences of −2.0 and +1.8 ppm for C1 and C4, respectively, relative to the C1/C4 chemical shift of the isolated model. Considering that this signal may be shifted by about −0.5 ppm with respect to the isolated E−N signal, owing to the small occurrence of a gauche conformer of dihedral $C\beta-C\alpha-C2-C3$ in the E−N copolymer, the expected chemical shifts for these two carbons in a P−N copolymer are 37.1 and 40.8 ppm, in good agreement with the two observed signals (Table 4).

Carbons C2/C3. These carbons show the largest chemical shift differences with respect to the isolated model. We notice that such a model, the *all-trans* conformer of 2,3-di-*n*-propylnorbornane, does not exactly represent the condition of carbons C2/C3 in an isolated N unit of E−N copolymers, since here dihedrals C2/3-$C\alpha-C\beta-C\gamma$ have a significant probability of being in a *gauche* conformation (say, ∼20%[4b]). Thus, chemical shifts predicted on the basis of computed differences relative to our model should be corrected by an amount of about +1./1.5 ppm. We notice that the differences between the chemical environments of the two carbons C2 and C3 have no analogy with the differences between C2 and C3 in the ENNE sequences (where the β-effect on C2 due to C1′ is balanced by the shielding γ effect due to the carbon bonded to C3′, in *syn* conformation with respect to C2, and by other interactions with N carbons). Here, the signal of C2 is shifted to low field primarily by the β-effect due to the presence of methyl $P\beta$; thus, in Table 3 for conformer *g′tttg* we find a difference of +6.35 ppm with respect to the isolated model. Some other conformers with φ_0 in the *t* state present shifts even larger than the most stable conformer, while the conformers with φ_0 in *g′* show similar differences. Finally, the conformer *tggtg* shows a much lower chemical shift (with a difference of −8.06 ppm with respect to the most stable conformer), arising from a strong γ-*gauche* interaction with atom $T\gamma$ (φ_4 is 49°) and probably from other ring interactions. Since this conformer, having a population of ∼0.03, is the only one affected by such a large negative shift, its effect is quite limited, so that a net average C2 shift of +6.4 ppm with respect to the isolated model (corresponding to a shift of more than 7 ppm relative to the isolated C2/C3 E−N signal). Hence, we argue that only carbon C2 may be responsible for the signal observed at 53.33 ppm (i.e., shifted +7.7 ppm to low field from the isolated C2/C3 E−N signal) in the spectra of low norbornene content P−N copolymers.

On the other side of the ring, the chemical shift of carbon C3 may be affected by γ-*gauche* effects that depend on rotations φ_0 and φ_2 (Figure 4). The interactions of C3 depending on φ_2 are expected to shift the signal to high field with respect to the isolated C2/C3 E−N signal, owing to the addition of $P\gamma$ (e.g., see the observed difference between the CH chemical shifts of 2-methylpentane and 2,4-dimethylpentane[12]), while it is not possible to guess the effects on C3 of the interactions which depend on φ_0. The reference conformer *g′tttg*, with a computed difference of −3.77 ppm with respect to the isolated model, presents two γ-*gauche* interactions (with $P\beta$ and $P\gamma'$, respectively), but the size of this shift indicates that only one interaction (the latter one) is effective. This datum confirms the results of previous ab initio computations,[5] for example, on *gauche* conformers of di-*n*-propylnorbornane (DPN) and on norbornane dimers; the uneffectiveness of *gauche* interactions across φ_0 on C3 (while effective on C1) may be due to δ-effects of the *syn* substituents of C2 and C3.[13] The present statistics yields an average C3 shift of −2.2 ppm relative to the isolated model. Thus, the expected chemical shift of C3 in a P−N copolymer should fall about −1 ppm from the C2/C3 isolated E−N signal. This may justify the assignment to C3 of the CH peak observed at 45.61 ppm, shifted by +0.6 ppm from the C2/C3 E−N signal, but there is a significant discrepancy between predicted and experimental values.

Methyl Carbons. We take as a reference for the methyl carbons the chemical shift value of 20.67 ppm computed for the central methyl of 2,4,6-trimethylheptane (TMH) in the *tgtg* conformation. This methyl shows *one* γ-*gauche* interaction, so that its signal should be shifted by no more than −0.2 ppm with respect to the signal of the PP isotactic methyl, for which the statistics adopted here yields a γ-*gauche* probability of 0.963. In the most stable conformer of PSLP, carbon $P\beta$ presents two γ-*gauche* interactions: the first one with carbon $T\gamma$ depends on dihedral φ_4, while the second one with C3 is a function of φ_0. However, the chemical shift value of 21.42 ppm computed for $P\beta$ seems to correspond to one rather than two *gauche* effects, as if the interaction with C3 were uneffective or if other deshielding effects due to the interaction with the N ring were active. Also, several other conformers show a similar behavior. A notable exception is offered by conformer *g′tgtg*, with a relative shift of −8 ppm with respect to *g′tttg*, consistent with the double *gauche* interaction of $P\beta$ with C3 and C1. The average chemical shift is estimated as 22.05 ppm, i.e., +1.4 ppm with respect to TMH. This result justifies the assignment to $P\beta$ of the P−N peak observed at 21.24 ppm, shifted by +1.56 ppm from the major PP peak and having a peak area approximately equal to that of the major norbornene peaks.

As far as the other methyls are concerned, the results of Table 11 of paper 1 show chemical shift differences of 4.5−5 ppm between pairs $P\gamma/P\gamma'$and $P\delta/P\delta'$, consistent with standard γ-*gauche* effects. However, we have not used the chemical shifts computed for these PLSP methyls. We rather have analyzed the behavior of the total probability for a methyl of being in *gauche* conformation with respect to its γ CH's (P_G) as a function of the distance from the N rings. The results show P_G values ranging from 0.83 to 1.00, corresponding to rather small shifts from the isotactic polypropylene signal (say, from −0.2 to +0.6 ppm). The highest P_G value is computed for methyl $P\gamma\delta$, while the lowest value is found for $P\epsilon\zeta$.

Other Carbons. The chemical shift calculations on model compound PLSP do not allow us to derive conclusions on the signals of most of the other propene carbons, since atoms $S\alpha$, $S\beta$, $T\beta$, and $T\gamma$ in this model lack the interactions with the continuing chain. We only notice that the average chemical shifts computed for $S\alpha$ and $S\beta$ differ by −4 ppm, a large difference that can hardly be overcome by the missing interactions, so that we should expect the $S\alpha$ signal to occur at higher field

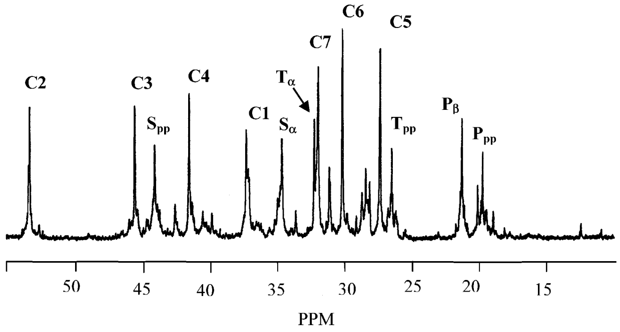

Figure 5. ^{13}C NMR spectrum of P−N copolymers prepared at [N]/[P] feed ratio 0.26 in the presence of **1**/MAO and final assignments as in Table 4. Chemical shifts are referred to HMDS: δ(HMDS) $\approx$ δ(TMS) −2.0 ppm.

than S_{PP}. The only other carbon whose computed average chemical shift should give indications for the P−N spectra is Tα. The MM2corr averaged value is 33.5 ppm, which is +2.5 ppm from the value computed for the central CH of the TMH model (in the *tgtg* conformation); such a difference is much smaller than the shift of the major T signal observed at 32.2 ppm with respect to T_{pp} (at 26.4 ppm). We also note that the average chemical shift computed for carbon T$\alpha\beta$ of the alternating P−N copolymer is 3.5 ppm greater than the above Tα value, i.e., about +6 ppm with respect to TMH.

Concerning the averages computed from the chemical shifts of the NPN model, we observe that, although the populations obtained with the two statistics appear quite different (last two columns of Table 6 of paper 1), the chemical shift averages show much smaller differences, and often the values almost coincide with the PSLP average: this holds for carbons C3, C4, C5, C6, and C7, while for the other carbons the two statistics show differences up to 1.5 ppm. Overall, these uncertainties are much smaller than the large shifts predicted between nonequivalent pairs of carbons (C5/C6, etc.). Finally, the average chemical shift for carbon S$\alpha\beta$, for which the difference due to statistics is 1.1 ppm, is about 4.5 ppm higher than the value computed for S$\alpha\beta$ of *meso* NEN, so that the signal should be expected around 33.5 ppm.

Final Assignments. The results discussed in the previous section along with DEPT experiments and comparisons with spectra of isotactic PP and E−N copolymers, allowed us to achieve a first detailed assignment of major signals of the P−N copolymer spectra, which are illustrated in Figure 5 and can be summed up as follows:

1. The two major CH_2 signals at 30.10 and 27.34 ppm have been assigned to C6 and C5, respectively. This assignment is justified from the weight-averaged chemical shifts of C6 and C5 computed ab initio, shifted by 1.5 and −1.0 ppm with respect to the isolated model, respectively. Secondary peaks around 28.3 ppm are present in some of the spectra and assigned to carbons C5/C6 of norbornene units connected to the chain via Sα on both sides.

2. Calculations agree very well with the assignment to carbon C7 of the major CH_2 signal observed at 31.91 ppm. Also, a minor peak is observed at 30.9 ppm arising from C7 of the CH_2−norbornene−CH_2 moiety.

3. The signals at 37.17 and 41.32 ppm have been assigned to C1 and C4, respectively. The average chemical shifts computed for C1 and C4 carbons yielded differences of −2.0 and +1.8 ppm for C1 and C4, respectively, relative to the C1/C4 chemical shift of the isolated model, in good agreement with the two observed signals.

4. The tertiary carbons at 45.40 and 53.32 ppm have been ascribed to C3 and C2, respectively. An average C2 shift of +6.4 ppm with respect to the isolated model (corresponding to a shift of more than 7 ppm relative to the isolated C2/C3 E−N signal) has been calculated. The predicted chemical shift of C3 in a P−N copolymer should fall about −1 ppm from the C2/C3 isolated E−N signal. This reasonably explains the assignment to C3 of the peak at 45.61 ppm, shifted by +0.6 ppm from the C2/C3 E−N signal.

5. The methyl Pβ peak observed at 21.24 ppm is shifted by +1.56 ppm from the major isotactic PP peak. The average chemical shift of +1.4 ppm with respect to TMH was estimated from ab initio calculations. According to the P_G calculations, no methyl signals are expected at lower field than 23 ppm.

6. Sα is expected at higher field with respect to S_{PP}. Therefore, we assign the major methylene signal at ~ 35 ppm to Sα. Tα is expected at lower field with respect to T_{PP}; hence, the first major tertiary carbon signal to the left of T_{PP} at 32.1 ppm is assigned to Tα.

Calculation of N Content. The above general assignments although not complete were used for a first calculation of norbornene incorporated in the P−N copolymers. The molar fractions of norbornene (f_N) and propene (f_P) can be calculated from the propene methyl signals or from norbornene signals by using the two following equations:

$$\frac{f_P}{7f_N + 3f_P} = \frac{I_{CH_3}}{I_{tot}} \tag{2A}$$

$$\frac{f_N}{7f_N + 3f_P} = \frac{1}{7}\frac{I_{C5,C6,C1,C4,C7,C2,C3}}{I_{tot}} \tag{2B}$$

where $f_P + f_N = 1$, I_{CH_3} is the observed peak area for propene methyl signals, $I_{C5,C6,C1,C4,C7,C2,C3}$ is the sum of the norbornene signals, and I_{tot} is the sum of the areas of all peaks. The two equations should give results comparable within the experimental error. However, the calculations, performed for a number of samples by assuming that each inserted propene unit gives rise to a methyl signal in the region between 15 and 22 ppm, show a great difference between the values of comonomer content derived from the two equations: the value of f_N obtained from the areas of norbornene signals being much smaller than the one calculated from the propene methyls. A typical example of such calculations for a copolymer prepared at [N]/[P] ratio of 0.07 is 35 N mol % from eq 2A and 19 N mol % from eq 2B. Inspection of the ratios between the CH and CH_2 peak areas suggests that eq 2A could overestimate the norbornene amount. Indeed, we have noticed that the total CH_2 peak area is in excess with respect to expected 3:4 ratio from norbornene and 1:1 from 1,2-propene inserted units. Such a CH_2 excess induced us to consider the existence of propene 1,3-misinsertions in the Mt−N bond as a possible source of the observed discrepancy.

In general, the total propene molar fraction would be due to the contribution of propene units in three different situations:

$$f_P = f_{P1} + f_{P2} + f_{P3} \tag{3}$$

Table 5. Norbornene Molar Fraction f_N, T_g, and Molar Mass (M_w) for Poly(P-*co*-N) Obtained with Catalysts 1 and 2 as a Function of [N]/[P] Molar Ratio in the Feed

					f_{P1}						
cat.	[N]/[P]	activity[a]	N conv (%)	f_N	$f_{P1,2}$	$f_{P2,1}$	f_{P2}	f_{P3}	T_g (°C)	M_w (g/mol)[c]	M_w/M_n[c]
1	0.05	164	8.32	0.16	0.70	0.01	0.11	0.02	19	14 752	2.68
1	0.07	107	9.29	0.25	0.55	0.03	0.16	0.01	37	11 118	1.21
1	0.10	70	5.56	0.23	0.56	0.01	0.19	0.01	47		
1	0.26	56	7.35	0.35	0.38	0.00	0.27	0.00	119	16 592	2.16
1	0.67	33	1.73	0.33	0.34	0.00	0.33	0.00	139	45 473	2.23
1	1.00	9	0.61	0.41	0.36	0.00	0.23	0.00	129	43 131	2.21
2	0.05	122	1.09	0.14	0.75	0.03	0.08	0.00	26	17 057	3.66
2	0.10	53	0.76	0.21	0.60	0.03	0.13	0.00	50	36 837	1.86
2	0.25	38	2.09	0.29	0.48	0.00	0.23	0.00	87	17 020	2.2
2	0.43	18	1.94	0.31	0.42	0.00	0.27	0.00			
2	0.67	8	0.04	(0.32)[b]	0.43	0.00	0.25	0.00	108	24 664	1.69
2	1.00	4		*b*					115	25 676	2.08

[a] Polymerization activity = (polymer kg/mol Zr h). [b] Quality and complexity of these spectra make difficult to estimate f_N of these samples. [c] Determined by a differential viscometer (DV).

where f_{P1} is the molar fraction of 1,2- or 2,1-inserted propene which gives rise to one methyl, one methylene, and one methine within the polymer chain; f_{P2} is the molar fraction of 1,3-misinserted propene which gives rise to three methylenes; and f_{P3} is the molar fraction of P units present as chain ends which give rise to one methyl and two methylenes as polymer chain ends.

The peak areas of all methyl (I_{CH_3}), methylene (I_{CH_2}), and methine (I_{CH}) signals are

$$\frac{I_{CH_3}}{I_{tot}} = \frac{f_{P1} + f_{P3}}{7f_N + 3f_P} = \frac{f_{P1} + f_{P3}}{7 - 4f_P} \tag{4}$$

$$\frac{I_{CH_2}}{I_{tot}} = \frac{3f_N + f_{P1} + 3f_{P2} + 2f_{P3}}{7f_N + 3f_P} = \frac{3f_N + f_{P1} + 3f_{P2} + 2f_{P3}}{7 - 4f_P} \tag{5}$$

$$\frac{I_{CH}}{I_{tot}} = \frac{4f_N + f_{P1}}{7f_N + 3f_P} = \frac{4f_N + f_{P1}}{7 - 4f_P} \tag{6}$$

With the help of DEPT spectra we are able to distinguish between methyl/methine and methylene signals, methyl resonances appearing at higher field with respect to those of methine (see Figure 4). Then by using eqs 3–6, we obtain a N content of 23 mol % for the sample which gave 35 from eq 2A and 19 from eq 2B.

On the other hand, it seems reasonable that by using eq 2B on the basis of the assignments of Table 4 only, one would underestimate the N content since the contributions from minor peaks are neglected. A more correct estimate would require spectra with higher signal resolution and a higher level of signal assignments. Extensions of assignments of N signals should take into account the contributions to the total N content of norbornene units present in sequences different from those containing isolated norbornene units PPNPP already considered. Thus, we consider the value of N content obtained by combining eqs 3–6 and DEPT information on the type of carbon signals as the most accurate estimate at the present level.

The results for six P–N copolymer samples prepared from a wide range of comonomer feed ratios in the presence of the catalyst precursor **1** are reported in Table 5. The norbornene content tends to level off around 40 mol %, even in the presence of a great norbornene excess. This is very much in contrast with literature report of P–N copolymers, prepared in the presence of catalyst **2**, showing N content linearly increasing with [N]/[P] ratio up to 98 mol %.[2] We wondered whether our result is due to the specific catalyst precursor used; therefore, we synthesized P–N copolymer samples in the presence of the catalyst precursor **2** under our experimental conditions. The results compared in the second part of Table 5 show that, at the temperature and monomer concentration used in our experiments, catalyst **2** allows for an even lower norbornene incorporation than **1**. These findings on the copolymer composition agree well with the thermal and molecular mass characteristics of the two copolymer series presented in the following section.

Molecular Mass and Glass Transition Temperature. Table 5 also lists molecular masses and glass transition temperatures (T_g) determined for the selected samples of poly(P-*co*-N). GPC molecular masses and polydispersities have been detected by both refractive index and viscometry since the determination of poly(E-*co*-N)s molecular mass showed that the polarity of the refractive index reverses at high norbornene copolymer content.[16] It is worth noting that M_W values of the P–N copolymers are quite low in comparison to those of E–N copolymers. The molecular mass might depend on the polymerization times; indeed, we found[15] that, under the same polymerization conditions used here, E–N polymerization with catalyst **1** is “quasi-living” for reaction times on the order of an hour. However, most P–N copolymer samples of Table 5 have polydispersity values close to those of a Schulz–Flory distribution ($M_w/M_n \approx 2$), probably owing to the long reaction times needed to collect enough polymer amount. The MM values are of the order of magnitude of those reported in the literature.[2]

High glass transition temperature (T_g) is an important characteristic of cycloolefin polymers; thus, T_g values of selected P–N polymer samples have been measured by DSC. Variations of norbornene content and T_g of copolymer samples vs [N]/[P] feed ratio are displayed in Figure 6. Such plots indicate that the values of both f_N and T_g for the P–N copolymers obtained with **1**/MAO and **2**/MAO increase quite sharply and seem to reach a plateau at a rather low [N]/[P]. In general, T_g values are rather low; this could be due to the low molar mass of the polymer samples as well as to a significant amount of propene 1,3-misinsertions. Indeed, the plots of T_g vs M_W of three samples prepared

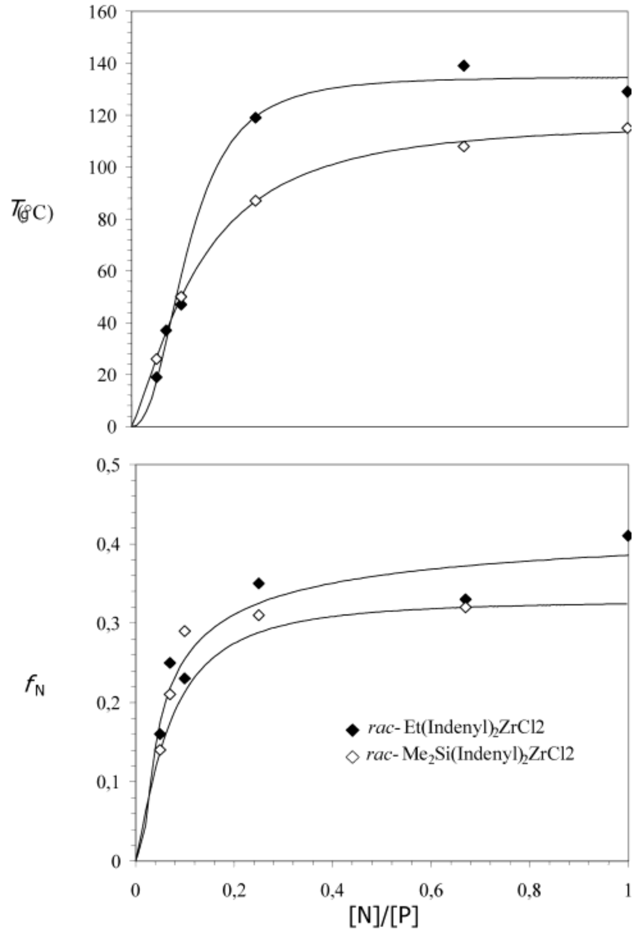

Figure 6. Plots of f_N and T_g for the P−N copolymers obtained.

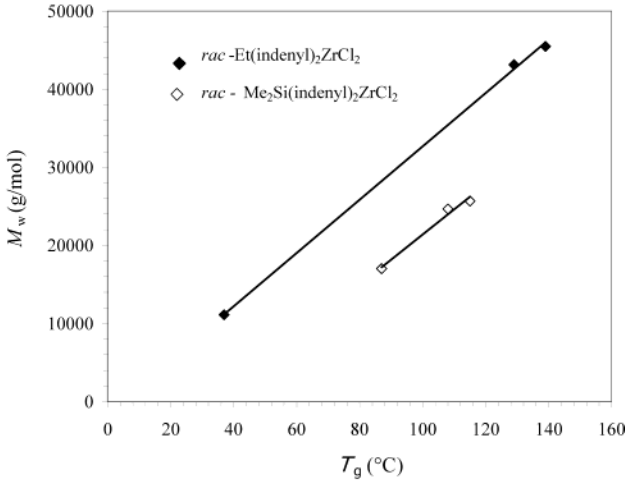

Figure 7. Plots of molar masses of the P−N copolymers, obtained with **1**/MAO and **2**/MAO, having the highest N content (see Table 5), as a function of glass transition temperature (T_g).

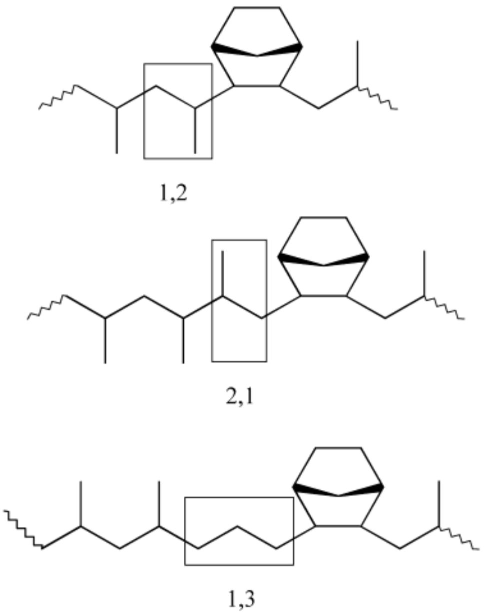

Figure 8. Possible 1,2-, 2,1-, and 1,3-propene insertions into the Mt−N carbon bond.

with each catalyst and having similar N incorporation show a significant, nearly linear dependence of T_g values on M_W (Figure 7). It is apparent that molecular masses of P−N copolymers are well below the plateau value above which T_g is not molar mass sensitive. The values of T_g of poly(E-*co*-N), for the same norbornene content, increases significantly up to a limit of M_W about 10 × 10^4 g/mol. Above this value, T_g remains practically constant. Interestingly, a sample of poly(E-*co*-N) prepared with a constrained geometry catalyst having 47.1% N and M_n of ∼4.3 × 10^4 g/mol displays a T_g value of 108 °C, that is, below the range of T_g values (129−139 °C) of E−N copolymers reported.[17]

Mechanistic Considerations. Inspection of the f_{P1}, f_{P2}, and f_{P3} values in Table 5 clearly shows a great amount of 1,3-propene misinsertion. The relative f_{P2}/f_{P1} ratio greatly increasing along with [N]/[P] feed ratio confirms our intuition that the origin of the low polymerization activity lies in the difficulty of inserting a propene in the Mt−tertiary carbon bond when N is the last inserted unit. Possible 1,2-, 2,1-, and 1,3-propene insertions into the Mt−N bond are sketched in Figure 8.

Such an environment seems to be so sterically crowded and low reactive as to cause almost one 1,3-misinsertion every other propene insertion at the low propene concentrations of high [N]/[P] feed ratios. This seems to be also the origin of the observed low molecular masses of P−N copolymers.

Conclusions

A first assignment of the main ^{13}C NMR signals of P−N copolymers containing isolated N units was given on the basis of DEPT ^{13}C spectra and by comparison with isotactic PP and E−N copolymer spectra. Ab initio theoretical ^{13}C NMR chemical shifts, computed for the most relevant conformers of a rather simple model compound and averaged over the RIS conformer populations estimated for an isotactic chain $(P_4{-}N)_x$, gave important detailed indications for the assignment of the complex ^{13}C spectra of P−N copolymers with N content up to 35 mol %.

Assignments allowed us to calculate the N copolymer content. A discrepancy was found between the values of norbornene content obtained from the areas of the major signals assigned to norbornene carbons and from the propene methyl signals appearing in the region between 15 and 22 ppm. To partially overcome such a discrepancy and the apparent excess of methylene over methine signal areas, the contribution of propene units arising from 2,1- and 1,3-misinsertions had to be considered for the calculation of copolymer composition.

1,3-Misinsertions are formed in significant amount as the [N]/[P] ratio of the feed increases.

Our results confirm that, despite the relatively lower polymerization activity, at low norbornene/olefin ratios it is possible to obtain P−N copolymers which are relatively richer in norbornene than the E−N copolymers prepared in similar conditions. It is conceivable that this could arise from the fact that norbornene competes more easily with propene than with ethene. However, at higher norbornene/olefin feed ratios the great amount of 1,3-propene misinsertions clearly reveals that the steric hindrance of the Mt−tertiary carbon bond when N is the last inserted unit makes difficult the next propene insertion, causing the low polymerization activities, molecular masses, and T_g.

Experimental Section

General Conditions. All experiments involving air-sensitive compounds were performed using standard glovebox and Schlenk techniques. **1**, **2**, and MAO were obtained from the Witco Co. **1** and **2** were used as received, MAO was dried under vacuum and stored as a powder, and toluene was distilled over sodium under a nitrogen atmosphere. Norbornene was distilled over potassium under a nitrogen atmosphere and used as a stock solution in toluene. Propene was passed over molecular sieves (4 Å) and BTS to remove oxygen and water.

Polymerization. To a thoroughly dried round-bottom flask (250 mL), toluene and norbornene stock solution were transferred to give the desired amounts of norbornene and a total liquid volume of 100 mL after addition of MAO and **1** or **2**. The stirring rate (700−1000 rpm) and propene pressure (1.01 atm) were set and kept constant during the runs, and equilibration was allowed. Finally, MAO (4 mmol) and catalyst (2 μmol), both dissolved in small amounts of toluene, were injected ([Al]/[Zr] = 2000). Polymerization was allowed for a period of time, from 0.5 to 4.00 h, to ensure low norbornene conversion before the polymer was precipitated in an ethanol (0.8 L)/HCl (10 mL) mixture, stirred overnight, filtered, stirred with ethanol overnight, filtered, and dried at 70 °C under vacuum.

^{13}C NMR. The copolymers were dissolved in $C_2D_2Cl_4$ with hexamethyldisiloxane (HMDS) as internal standard. The spectra were recorded on a Bruker AM-270 spectrometer operating at 67.89 MHz (^{13}C) in the PFT mode operating at 103 °C. Further experimental details were as reported earlier.[4c,d] ^{13}C DEPT NMR spectra were measured with composite pulse decoupling using the sequence $\tau_1-90°-\tau_2-180°$, $90°-\tau_2-135°$, $180°-\tau_2-$CPD−acquire, with delays τ_1 of 21 s, τ_2 of 4.0 ms and 90° pulse widths of 10.1 and 18 μs for ^{13}C and ^{1}H, respectively.

Size Exclusion Chromatography. The molar mass distribution (MMD) and polydispersity were performed on a high-temperature dual-detector size exclusion chromatography (SEC) system. The SEC system was a GPCV2000 from Waters (Milford, MA) that uses two on-line detectors: a differential viscometer (DV) and a differential refractometer (DRI) as concentration detector. The description of this SEC−DV system has been reported elsewhere.[18] The experimental conditions were as follows: *o*-dichlorobenzene + 0.05% 2,6-di-*tert*-butyl-4-methylphenol (BHT, antioxidant) as mobile phase, 0.8 mL/min as flow rate, and a column temperature of 145 °C. The column set was composed of three GMH$_{XL}$-HT columns from TosoHaas (Stuttgart, Germany). The universal calibration was constructed from 18 narrow MMD polystyrene standards, with the molar mass ranging from 162 to 5.48×10^6 g/mol. The MM values reported in Table 5 are those obtained with the DV detector.

DSC. DSC measurements were performed using a Perkin-Elmer Pyris 1 equipped with signal subambient devices. The copolymer sample (3−6 mg) was first cooled to −80 °C and kept there for 1 min. Then the sample was heated to 200 °C (20 °C/min), cooled to −80 °C (20 °C/min), and heated to 200 °C (20 °C/min). The sample was kept under a He flow (30 mL/min) during the whole run, and the glass transition temperature, T_g, was taken from the second heating.

Acknowledgment. Financial support from EC TMR Project Network No. ERB FMRX CT97-0116 GLASSCYCLICS is gratefully acknowledged. We thank Mr. A. Giacometti Schieroni for his cooperation with the SEC analysis.

References and Notes

(1) Kaminsky, W.; Bark, A.; Arndt, M. *Macromol. Chem. Macromol. Symp.* **1991**, *47*, 83. (b) Cherdron, H.; Brekner, M.-J.; Osan, F. *Angew. Makromol. Chem.* **1994**, *223*, 121. (c) Arndt, M.; Kaminsky, W. *Macromol. Symp.* **1995**, *97*, 225.

(2) Henschke, O.; Köller, F.; Arnold, M. *Makromol. Rapid Commun.* **1997**, *18*, 617.

(3) Kaminsky, W.; Arndt-Rosenau, M. In *Metallocene-based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; p 89 and references there.

(4) Tritto, I.; Boggioni, L.; Sacchi, M. C.; Locatelli, P. *J. Mol. Catal. A: Chem.* **1998**, *133*, 139. (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.; Brintzinger, H. H.; Ferro, D. R. *Macromolecules* **2001**, *34*, 5770.

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

(6) Carbone, P.; Ragazzi, M.; Tritto, I.; Boggioni, L.; Ferro, D. R *Macromolecules* **2003**, *36*, xxxx.

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

(8) Tritto, I.; Boggioni, L.; Jansen, J.; Thorshaug, K.; Sacchi, M. C.; Ferro, D. R. *Macromolecules* **2002**, *35*, 616.

(9) For selectivity and reactivity in propene polymerization with metallocene catalysts, see: Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253 and references therein.

(10) Arndt, M.; Engehausen, R.; Kaminsky, W.; Zoumis, K. *J. Mol. Catal. A: Chem.* **1995**, *101*, 171.

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

(12) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

(13) We can take the chemical shifts of C3 in Table 3 as an example to illustrate to what extent the differences computed ab initio among the conformers can be rationalized in terms of γ-*gauche* interactions. The small dependence of the C3 chemical shift on rotations (φ_3, φ_4) is seen if the values computed for items **1**, **3**, and **2** are compared with those of **7** and **b**, of **a**, and of **8**, respectively. There are four states for the pair of dihedrals (φ_3, φ_4); items **4** and **d**, compared with **1** and **3**, respectively, show that the γ-*gauche* effect with Pγ' nearly disappears in state (t^+t), owing to a syn-δ interaction; item **6** indicates a slightly stronger interaction with Pγ in state ($g't$); and comparison of the last three items (**9** and **c** with **1**, and **e** with **3**) shows a negative shift of about −4 ppm associated with the double the γ-*gauche* effect in state (t^+g'). Finally, it is not possible to interpret the positive shifts of about 2.5 and 3.5 ppm found in the conformers where φ_0 is in states g' and g, respectively.

(14) Carvill, A.; Zetta, L.; Zannoni, G.; Sacchi, M. C. *Macromolecules* **1998**, *31*, 3783.

(15) Jansen, J. C.; Mendichi, R.; Locatelli, P.; Tritto, I. *Macromol. Rapid Commun.* **2001**, *22*, 5770.

(16) Bergström, C. H.; Seppälä, J. V. *J. Appl. Polym. Sci.* **1997**, *63*, 1063. (b) Thorshaug, K.; Mendichi, R.; Tritto, I.; Trinkle, S.; Friedrich, C.; Mulhaupt, R. *Macromolecules* **2002**, *35*, 2903.

(17) Ekizoglou, N.; Thorshaug, K.; Cerrada, M. L.; Benavente, R.; Pérez, E.; Pereña, J. M. Submitted to *Polymer*.

(18) Brun, Y.; Nielson, R.; Tacconi, R. *Proc. Int. GPC Symp. '98, Phoenix, AZ* **1998**, 415.

MA0212487