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The Conformational Characteristics of Ethylene−Norbornene Copolymers and Their Influence on the ^{13}C NMR Spectra

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ABSTRACT: A rotational-isomeric-state treatment of ethylene−norbornene copolymers has been worked out for the purpose of establishing a correlation between conformation and ^{13}C NMR chemical shifts of this new class of polymers and of clarifying their microstructure. A comparison of conformer populations computed for the stereoregular alternating $(N-E)_x$ chains and for copolymers including such defects as N−N, E−E, E−E−E, and N−N−N indicates the need for accounting for the tacticity of the chain, besides its composition, in the interpretation of the spectra. Some stereochemical shifts were suggested by the calculations. In particular, conformational analysis predicted and evidenced the origin of distinct *meso/racemic* signals for methines C2 and C1 and for the ethylene carbon of the regularly alternating copolymers. This prediction induced a more thorough analysis of the ^{13}C NMR spectra of mainly alternating $(N-E)_x$ copolymers, allowing us to recognize and distinguish *isotactic* and *syndiotactic* N−E−N sequences. Then, a detailed and unambiguous assignment of the spectra of stereoregular and irregular alternating E−N copolymers was achieved. The strong effect of ring distortions in the presence of N−N dyads and triads is also discussed.

Introduction

Ethylene−norbornene copolymers,[1−3] obtained with metallocene-based catalysts, form a new class of polymers of practical interest since they are endowed with good mechanical and optical properties. Their synthesis is made possible by some of the unique characteristics the newly developed metallocene-based catalysts for olefin polymerization have with respect to the traditional heterogeneous catalysts. They typically lead to uniform chains of ethylene−α-olefin copolymers in which comonomers are randomly distributed, and they are able to polymerize cyclic olefins without ring-opening metathesis. Catalysts for addition polymerization of norbornene based on Pd(II)[4,5] and Ni[6] have also been developed in recent years. Metallocene catalysts make possible the synthesis of a variety of ethylene−norbornene copolymers,[1−3,7] which were first reported by Kaminsky[1] and in Hoechst patents.[8] Their excellent clarity and high glass transition temperatures when they have high norbornene content make these materials able to compete with polycarbonates and polymethylmetacrilates. Such properties depend on composition and comonomer distribution in the chain; hence, a significant effort is being devoted to clarifying the microstructure of E−N copolymers by means of ^{13}C NMR spectroscopy.[7b,9−12] However, a complete understanding of the mechanisms involved in these copolymerizations, as well as of the relationship between copolymer composition and properties of the materials, has not been achieved so far. This is partially due to the incompleteness of the characterization, owing to the complexity of the ^{13}C NMR spectra of the E−N copolymers. A second serious difficulty arises from the lack of knowledge concerning the (average) conformation of these copolymer chains.

Scarce attention has been paid so far to conformational analysis of norbornene polymers and copolymers. Haselwander et al.[13,14] performed detailed molecular mechanics and dynamics simulations of polynorbornene in order to compute conformational properties (end-to-end distance, radius of gyration, etc.) but, rather surprisingly, ignored the *meso/racemic* relationships between adjacent units, de facto considering only the syndiotactic homopolymer (Figure 4 of ref 13). Molecular modeling was also utilized in studies[10] of the interactions between the catalyst and polynorbornene growing chain in order to clarify the chain microstructure. However, there is the need for elucidating the conformation of this class of polymers and copolymers as a function of composition and configuration of the chain.

Molecular modeling may help close the gaps concerning microstructure and structure/properties relationship, by calculating average conformational properties of these copolymers in general and specifically by establishing the correlation between molecular conformation and ^{13}C chemical shifts. In the past we have been able to rationalize the chemical shifts of stereoirregular polymers (polypropylene in primis),[15,16] by recognizing (empirically) specific conformational effects observed in chemical shifts of model compounds, such as the well-known γ-gauche effect, and by weighing such effects by means of the statistical analysis of the chain conformation.

We set up a project for determining the conformational characteristics of polynorbornenes and ethylene−norbornene copolymers on the basis of molecular mechanics, with the major purpose of helping the interpretation of their ^{13}C NMR spectra. Here we present the results obtained for regularly alternating (*isotactic* and *syndiotactic*) E−N copolymers, and for the same copolymers containing one such defect as −E−E−, −E−E−E−, −N−N−, or −N−N−N− sequences. In the present study we have first determined the conformer populations, in the rotational-isomeric state (RIS) approximation,[17] at each distinct bond of the chain. Second, we have established a correlation between the computed populations and the observed chemical shifts. As mentioned above, such an interpretation of stereochemical shifts is based on the statistical evaluation of effects associated with gauche interactions. Hence, the results

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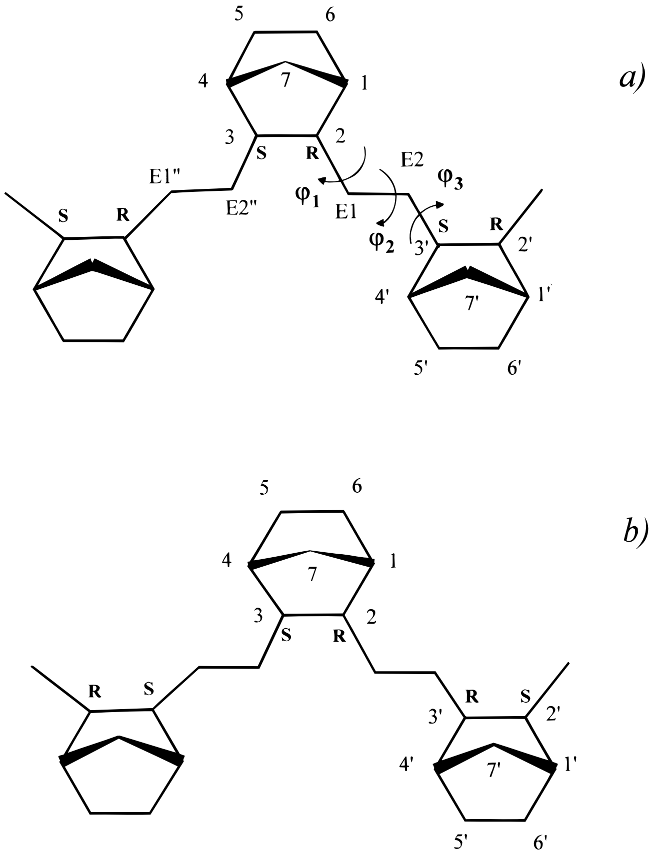

Figure 1. Segments −N−E−N−E−N− of *S*/*R*−*S*/*R*−*S*/*R* isotactic (a) and *R*/*S*−*S*/*R*−*R*/*S* syndiotactic (b) alternating ethylene−norbornene copolymers. For simplicity, ring carbons C1, C2, etc., in the figures are indicated as 1, 2, etc. The three dihedral angles φ_1(C3−C2−E1−E2), φ_2(C2−E1−E2−C3′), and φ_3(E1−E2−C3′−C2′) define the conformation of a N−E−N unit.

obtained for the present model of the E−N chain will be mostly presented and discussed in terms of gauche conformer populations (or gauche content) at the various bonds of the chain. Finally, the prediction of stereochemical shifts and a deeper analysis of the spectra allowed us to identify the presence of isotactic and syndiotactic sequences in mainly alternating E−N copolymers.

Conformational Analysis

1. Method of Calculation. Figure 1 shows the segments N−E−N−E−N for both isotactic and syndiotactic alternating copolymers.

According to the experimental findings, we only consider the *exo*−*exo* ring attachment, so that the configuration at atoms C2/C3 in a ring can only be *S*/*R* or *R*/*S*; we call *m* (*meso*) the relationship between two successive rings having the same configuration and *r* (*racemic*) the relationship between rings with opposite configuration. The conformation of a repeating unit is defined by the three dihedrals φ_1(C3−C2−E1−E2), φ_2(C2−E1−E2−C3′), and φ_3(E1−E2−C3′−C2′). A more complete description should account for the distortion of the ring, described for example by dihedral E2″−C3−C2−E1 (ψ) or by C4−C3−C2−C1; however, preliminary calculations have shown that in alternating copolymers distortions play a minor role.

To account for the deviations from the staggered conformers *t*, *g*, and *g*′, we started by defining nine conformational states for each dihedral φ (*t*−, *t*, *t*+, *g*, *g*+, *s*, *g*′, *g*′−, and *s*′, corresponding to the ranges 120/150/−150/−120/−90/−69/0/69/90/120°). The first step was the search of all distinct energy minima for a number of model compounds. For the alternating copolymers we utilized the models met−(N−E−)$_x$ −N−met, with *x* varying from 1 to 4, mainly considering the all-*m* and all-*r* configurations. The analysis of the results of these computations gave three types of indications, which determined the subsequent steps of the work, concerning: (a) definition of the RIS states; (b) energy additivity of the RIS states; (c) choice of force field.

Table 1. Major Conformational States for Isotactic and Syndiotactic E−N Alternating Copolymers, Referred to Repeating Units *S/R*−*S/R* and *S/R*−*R/S*, Respectively[a]

isotactic					syndiotactic				
RIS	φ_1	φ_2	φ_3	pop.	RIS	φ_1	φ_2	φ_3	pop.
1	t	t	t	0.608	1	t	t	t	0.603
2	t	t	*g*+	0.158	2	t	t	*g*+	0.006
3	*g*′−	t	t	0.158	3	*g*+	t	t	0.006
4	t	t	*g*′−	0.006	4	t	t	*g*′−	0.097
5	*g*+	t	t	0.006	5	*g*′−	t	t	0.097
6	*g*′−	t	*g*′−	0.001	6	*g*′−	t	*g*′−	0.016
7	*g*+	t	*g*+	0.001	8	*g*′−	t	*g*+	0.001
8	*g*′−	t	*g*+	0.001	9	*g*+	t	*g*′−	0.001
10	t	g	*t*−	0.011	10	t	g	t	0.166
11	*t*+	g′	t	0.011	16	t	*g*+	*s*′	0.001
14	t	g^+	*g*+	0.015	17	*s*′	*g*+	t	0.001
15	*g*′−	*g*′−	t	0.015	18	*g*′−	g′	*g*′−	0.003

[a] Conformer populations were computed at 100 °C using the MM3 force field with solvent contribution ($CHCl_3$).

(a) Definition of the RIS States. Inspection of hundreds of conformers in compounds of growing length shows the persistence of a limited number of conformational patterns *i* of the repeating unit, described by a triplet of values $(\varphi_1, \varphi_2, \varphi_3)_i$ of the dihedrals. Hence such patterns rather than the individual bond conformers were chosen as RIS states to be used for the chain statistics. We found 27 such states both for the isotactic and the syndiotactic chain, but only 21 were used and a much smaller number contribute significantly to the conformer population; the 12 most stable states are described in Table 1.

(b) Energy Additivity of the RIS States. The conformational energy of a chain of *l* repeating units is assumed to be

$$E = {}^1/_2E_1(i_1) + \mathbf{U}(i_1,i_2) + \mathbf{U}(i_2,\, i_3) + ... \mathbf{U}(i_{l-1},\, i_l) + {}^1/_2E_1(i_l) \quad (1)$$

where i_k represents the state of unit *k*

$$U(i,j) = E_2(i,j) - {}^1/_2E_1(i) - {}^1/_2E_1(j)$$

and E_1 and E_2 are the energies of met−(N−E−)$_x$−N−met, computed for $x = 1$ and 2, respectively.

Equation 1 implies that there is no correlation between nonnearest neighboring units: compounds with $x = 3$ and 4 were then used to check such an assumption of additivity. When computations are performed for isolated molecules (in vacuo) two families of conformers are found: while for the larger family additivity holds with very good approximation (errors of less than 0.1 kcal/mol), a small number of conformers (showing a rather compact shape) present large (negative) deviations, up to 3 or 4 kcal/mol. However, when a solvent contribution is included in the energy function, in the approximation of the continuum medium, the discrepancies between the energies actually computed for the long chains and the values obtained using eq 1 greatly decrease also for the second type of conformers. This proves that the conformational states *i* are well defined, maintaining their identity in all compounds, while the simulated solvent effect balances the attractive interactions between nonneighboring units in compact conformers. Thus, use of eq 1 for computing the partition function of an infinite chain and the conformer populations appears to be justified. We also note that populations derived from eq 1 using energies computed with or without solvent are quite similar.

Equations similar to (1) were obtained in order to compute partition function and conformer populations when a single defect is inserted in the alternating E−N copolymer, by replacing a central matrix $\mathbf{U}(i,j)$ with the appropriate matrix $\mathbf{U}'$ representing the defect. This required other series of energy minima searches for the following model compounds: met−N−E−Et, Et−E−N−E−Et; met−N−E−N−E−Et (*m* and *r*); met−N−E−E−N−met (*m* and *r*); met−N−E−E−E−N−met (*m*); met−N−E−N−N−E−N−met (*mMm*, *mRm*, *rMr*, and *rRr*); met−N−E−N−N−N−E−N−met (*mMMm*, and *mRRm*).

In −N−N− or in −N−N−N− sequences we call *M* the relationships between rings with the same configuration and *R* those between rings with opposite configurations. RIS states for the N−E−E segment were defined in a manner similar to N−E−N, while for N−N dyads a further single-bond state was defined.

(c) Choice of Force Field. Both Allinger's force fields MM2[18] and MM3[19] were adopted for the present calculations. The two potentials yield very close conformations of minimum energy (differences of few degrees) and lead in practice to the same definition of RIS states. However, some significant differences are found with regard to the relative stabilities of a few important conformers (on the order of 0.5 kcal/mol), which lead to differences in conformer populations for φ_1 and φ_3. For the moment, we choose to use MM3, which represents an upgrade of MM2, throughout this work, but also other force fields should be applied in the future for a comparison.

The computations were carried out using programs CHAMP/93,[20] developed in this laboratory, and Macromodel,[21] on workstations Silicon Graphics IRIS 4D/320GTX and SUN 20/61.

2. Conformer Populations. Perfectly Alternating N−E Copolymers. The major conformational states determined for isotactic and syndiotactic E−N alternating copolymers, referred to repeating units *S*/*R*−*S*/*R* and *S*/*R*−*R*/*S*, respectively, and the conformer populations computed at 100 °C are reported in Table 1. The average dihedral values and the populations of single conformers φ_1(C3−C2−E1−E2) and φ_2(C2−E1−E2−C3′) in the same isotactic and syndiotactic E−N alternating copolymers are listed in Table 2.

The insertion of an ethylene molecule between two norbornene units is expected to release much of the intramolecular strain, making the chain less rigid than polynorbornene, but the degree of flexibility turns out to be rather limited, as only few RIS states contribute significantly to the populations, listed in the third and sixth columns of Table 1. Indeed, we find that for both isotactic and syndiotactic copolymers the all-anti (*t t t*) state represents 60% of the population and five or six states account for 97% of the total. This is evident also in Table 2, where the populations of the individual conformers are listed with the corresponding average dihedrals $\langle\varphi\rangle$ (note that $\langle\varphi_3\rangle$ is related to $\langle\varphi_1\rangle$ by symmetry). The major difference between the two copolymers is due to the presence of the (*t g t*) state in the syndiotactic copolymer (shown in Figure 2b), which accounts for a significant population of the gauche conformer at the central bond (0.17 compared with 0.05 for isotactic N−E). A second difference is represented by a higher amount of *t* at φ_1 for the syndiotactic copolymer.

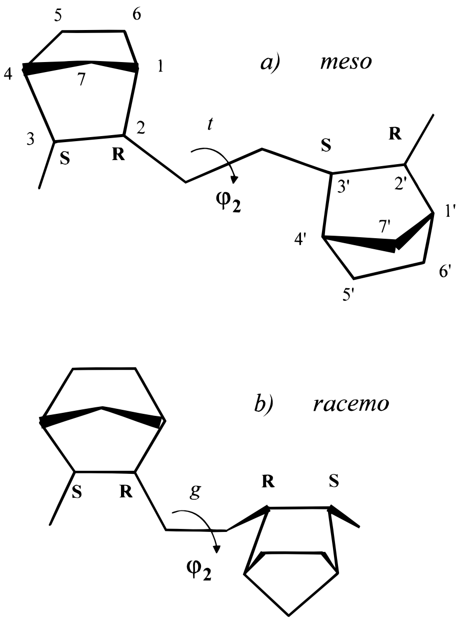

Figure 2. Two N−E−N conformers: (*a*) the all-anti conformation of the *meso* unit; (*b*) the *t g t* conformation, present significantly only in the *racemic* unit.

Table 2. Average Dihedral Values (deg) and Populations of Single Conformers φ_1 (C3−C2−E1−E2) and φ_2 (C2−E1−E2−C3′) in Isotactic and Syndiotactic E−N Alternating Copolymers, Referred to Repeating Units *S/R*−*S/R* and *S/R*−*R/S*, Respectively

	isotactic				syndiotactic			
	φ_1		φ_2		φ_1		φ_2	
conf.	av	pop.	av	pop.	av	pop.	av	pop.
t−								
t	−173.6	0.798	180.0	0.948	−176.0	0.872	172.6	0.826
t+	−155.4	0.010			−155.4	0.002		
s'	−107.8	0.001			−109.2	0.002		
g′−	−82.0	0.184	−74.5	0.015	−81.4	0.118	−84.8	0.002
g′			−64.1	0.011			−52.4	0.004
g			64.1	0.011			54.4	0.166
g+	75.6	0.007	74.5	0.015	77.7	0.006	70.9	0.009
s								

Defects in Alternating N−E Copolymers. Results of the computations on the same copolymers containing −E−E−, −E−E−E−, −N−N−, or −N−N−N− sequences as defects are reported in Tables 3−7. For brevity, for these and for the following calculations, we omit a detailed conformational description as in Tables 1 and 2, but we summarize the results in terms of gauche content at each dihedral, in view of the discussion on the correlation between conformation and chemical shifts. Table 3 reports the gauche populations for the N−E bonds inside the N−E−N unit adjacent to the defect, in comparison with the perfectly alternating copolymers. Similarly, Table 4 shows the populations

Table 3. Average Dihedral Values (deg) and Gauche Populations at N−E Bonds in the N−E−N Unit Adjacent to Defects in Various E−N Copolymers, Referred to Configurations *S/R*−*S/R* and *S/R*−*R/S*, Respectively, for *m* and *r* Units[a]

		φ_1(C3−C2−E1−E2) conformer *g*′		φ_1*(C1−C2−E1−E2) conformer *t*		φ_3(E1−E2−C3′−C2′) conformer *g*		φ_3*(E1−E2−C3′−C4′) conformer *t*	
entry	confign[c]	av	pop.	av	pop.	av	pop.	av	pop.
				Regularly Alternating (N−E)					
1a	isot	−82.0	0.184	69.4	0.808	82.0	0.184	−69.4	0.808
1b	synd	−81.4	0.118	66.8	0.874	−81.4	0.118	66.8	0.874
				$(-N-E)_x-N-E-E-(N-E-)_x$[b]					
2a	isot *meso*	−80.5	0.201	69.9	0.792	83.3	0.162	−68.8	0.828
2c	synd *meso*	−80.3	0.122	67.2	0.872	−83.0	0.096	66.2	0.893
				$(-N-E)_x-N-E-E-E-(N-E-)_x$[b]					
3a	isot *meso*	−80.5	0.200	69.9	0.792	83.2	0.164	−68.8	0.826
3c	synd *meso*	−80.3	0.122	67.2	0.872	−83.0	0.097	66.2	0.892
				$(-N-E)_x-N-N-(E-N-)_x$					
5a	isot *meso*	−79.0	0.022	70.0	0.974			−69.6	0.945
5b	isot *rac*	−80.7	0.134	69.4	0.860	87.1	0.002	−72.2	0.985
5c	synd *meso*	−80.4	0.118	66.8	0.873			63.5	0.991
5d	synd *rac*	−81.7	0.090	66.8	0.901	88.0	0.001	69.6	0.993
				$(-N-E)_x-N-N-N-(E-N-)_x$					
6a	isot *MM*	−77.1	0.009	69.3	0.967	84.6	0.011	−69.7	0.955
6b	isot *RR*	−80.2	0.002	68.6	0.976	81.2	0.010	−72.5	0.920

[a] One conformer (*g* in the case of φ_1, where E2 is in the gauche position with respect to both C3 and C1) gives always negligible contributions, which for clarity have been omitted in all tables. [b] The same values are found also for the *racemic* configuration. [c] Key: isot, isotactic; synd, syndiotactic.

Table 4. Average Dihedral Values (deg) and Gauche Populations at N−E Bonds in Defects N−E−E−N and N−E−E−E−N of E−N Copolymers, Referred to Configurations *S/R*−*S/R* and *S/R*−*R/S*, Respectively, for *m* and *r* Units

		φ_4(C3′−C2′−E11−E12) conformer *g*′		φ_4*(C1′−C2′−E11−E12) conformer *t*	
entry	confign[a]	av	pop.	av	pop.
		$(-N-E)_x-N-E-E-(N-E-)_x$			
2a	isot *meso*	−83.5	0.145	67.2	0.847
2b	isot *rac*	−83.5	0.134	66.9	0.858
2c	synd *meso*	−83.0	0.122	67.5	0.843
2d	synd *rac*	−83.0	0.122	67.3	0.853
		$(-N-E)_x-N-E-E-E-(N-E-)_x$			
3a	isot *meso*	−83.5	0.135	67.0	0.858
3b	isot *rac*	−83.5	0.133	67.0	0.859
3c	synd *meso*	−83.0	0.140	67.4	0.853
3d	synd *rac*	−83.0	0.139	67.4	0.855
		$(N-E-E-E-)_x$			
4a	isot	−83.3	0.132	67.3	0.861
4b	synd	−83.3	0.131	67.3	0.862

[a] Key: isot, isotactic; synd, syndiotactic.

at N−E bonds in defects N−E−E−N and N−E−E−E−N, while the data concerning ethylene bonds are presented in Table 5. Gauche populations at N−N bonds in dyad and triad defects of E−N copolymers are shown in Table 6. Table 7 lists the conformations and ring distortions of the lowest-energy minima of several model compounds of E−N copolymers. In all stereoisomers, the configuration of the first ring is *S*/*R*. Relative conformational energies are expressed in kcal/mol.

(a) Effect of E−E Defects. Addition of other ethylene units in alternating N−E copolymers obviously greatly increases the chain flexibility. The purpose of various computations was to evaluate the effects of the addition on the adjacent N−E−N unit (see Figure 3), as well as to observe the gradual approaching of the $-CH_2-$ moiety to the polyethylene state.

Concerning the gauche populations for the N−E bonds inside the N−E−N unit adjacent to the defect (Table 3), the results show that an E−E defect produces quite small differences in the adjacent N−E−N unit, which keeps its *m* or *r* characteristics independent of the tacticity of the defect; there is only a modest increase of the gauche content for φ_1 and φ_2, and a decrease for φ_3. This confirms the rigidity of the chain, and excludes the possibility that appreciable effects may be found on farther units. The gauche probability at φ_4 in a N−E−E−N defect (Table 4) is intermediate between those found for *m* and *r* regular units and is barely dependent on the tacticity of the defect and of the copolymer in which the defect is inserted. The bottom row of Table 4 indicates the conformation to which an isolated norbornene unit embedded in polyethylene converges.

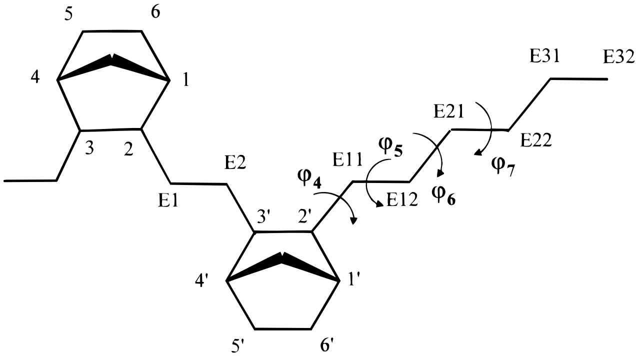

Figure 3. N−E−E−E− defect adjacent to a regular N−E−N unit.

We found that the N−E−E− defect (Table 5) produced larger effects on the conformation at the CH_2-CH_2 bond closest to N (φ_5), where still only one gauche conformer is practically present, but with a significant population independently of the tacticity (compare entries 2a, 2b, ...). Thus, addition of an E unit nearly eliminates the major *m*/*r* difference found in the regular copolymers. Addition of another E has no effect on φ_5 (compare 3a and 3b), while the total gauche content quickly increases for the farther CH_2-CH_2 bonds, so that the conformation for φ_7 can be assimilated to that of polyethylene.

(b) Effect of N−N Dyads. Such defects, sketched in Figure 4, induce steric strain in the E−N chain, as shown by deformations of the norbornene ring (Table

Table 5. Average Dihedral Values (deg) and Gauche Populations at E−E Bonds in Various E−N Copolymers, Referred to Configurations *S/R*−*S/R* and *S/R*−*R/S*, Respectively, for *m* and *r* Units

		φ_2(C2−E1−E2−C3′)				φ_5(C2′−E11−E12−E21)				φ_6(E11−E12−E21−E22)				φ_7(E12−E21−E22−E31)			
		conformer *g*′		conformer *g*		conformer *g*′		conformer *g*		conformer *g*′		conformer *g*		conformer *g*′		conformer *g*	
entry	confign[a]	av	pop.	av	pop.	av	pop.	av	pop.	av	pop.	av	pop.	av	pop.	av	pop.
Regularly Alternating (N−E)																	
1a	isot	−70.1	0.026	70.1	0.026												
1b	synd	−52.4	0.004	54.6	0.168												
$(-N-E)_x-N-E-E-(N-E-)_x$																	
2a	isot *meso*	−70.0	0.032	71.3	0.029	−71.1	0.036	60.5	0.178	−64.4	0.164	64.4	0.164				
2b	isot *rac.*	−70.0	0.032	71.0	0.030	−71.3	0.031	60.2	0.200	−66.5	0.117	62.2	0.233				
2c	synd *meso*	−53.7	0.004	54.2	0.176	−70.6	0.038	60.6	0.174	−64.4	0.163	64.4	0.163				
2d	synd *rac.*	−53.7	0.004	54.2	0.176	−70.9	0.032	60.3	0.195	−66.5	0.115	62.2	0.231				
$(-N-E)_x-N-E-E-E-(N-E-)_x$																	
3a	isot *meso*	−70.0	0.032	71.0	0.030	−69.1	0.033	60.6	0.177	−64.9	0.136	63.3	0.195	−63.5	0.157	63.5	0.157
3b	isot *rac.*	−70.1	0.032	71.1	0.029	−69.2	0.032	60.8	0.180	−65.2	0.131	63.2	0.203	−64.1	0.137	63.1	0.181
3c	synd *meso*	−53.7	0.004	54.2	0.176	−70.9	0.033	60.6	0.173	−64.9	0.135	63.4	0.194	−63.6	0.157	63.6	0.157
3d	synd *rac.*	−53.7	0.004	54.2	0.176	−69.2	0.033	60.8	0.175	−65.3	0.130	63.2	0.202	−64.1	0.138	63.1	0.181
$(N-E-E-E-)_x$																	
4a	isotactic					−70.0	0.033	60.5	0.176	−64.9	0.134	63.3	0.194	−63.6	0.157	63.6	0.157
4b	syndiotactic					−70.1	0.032	60.6	0.179	−65.3	0.129	63.2	0.203	−64.1	0.137	63.1	0.182
$(-N-E)_x-N-N-(E-N-)_x$																	
5a	isot *meso*	−62.3	0.030	64.3	0.047												
5b	isot *rac.*	−70.2	0.033	63.6	0.011												
5c	synd *meso*	−67.3	0.005	53.1	0.234												
5d	synd *rac.*	−63.0	0.003	56.5	0.198												
$(N-E)_x-N-N-N-(E-N-)_x$																	
6a	isot *MM*	−54.4	0.009	64.5	0.014												
6b	isot *RR*	−67.5	0.001	64.1	0.009												

[a] Key: isot, isotactic; synd, syndiotactic.

Table 6. Average Dihedral Values (deg) and Gauche Populations at N−N Bonds in Dyad and Triad Defects of E−N Copolymers, Referred to Configurations *S/R*−*S/R* and *S/R*−*R/S*, Respectively, for *m* and *r* Units

		φ_4(C3′−C2′−C3″−C2″)		φ_4*(C1′−C2′−C3″−C2″)		φ_4*(C3′−C2′−C3″−C4″)		φ_4**(C1′−C2′−C3″−C4″)	
entry	confign[a]	av	pop.	av	pop.	av	pop.	av	pop.
$(-N-E)_x-N-N-(E-N-)_x$									
5a	isot *meso*			61.1	1.0	−61.1	1.0		
5b	isot *rac.*	−73.3	1.0					51.1	1.0
5c	synd *meso*			61.1	1.0	−61.1	1.0		
5d	synd *rac.*	−73.3	1.0					50.8	1.0
$(-N-E)_x-N-N-N-(E-N-)_x$									
6a	isot *MM*	−73.3	0.165	55.7	0.808	−58.5	0.526	−62.7	0.165
						−74.7	0.309		
						61.4	0.165		
6b	isot *RR*	−77.6	0.490	82.9	0.494	84.3	0.494	45.8	0.500
								−39.1	0.500

[a] Key: isot, isotactic; synd, syndiotactic.

7). The strain is larger for *meso* than for *racemic* dyads: energy differences on the order of 3 kcal/mol are found between the most stable conformers of model compounds differing only for the dyad configuration (compare the energies of the most stable conformers of *mMm* and *mRm* of met−NENNEN−met). The effect on the adjacent N−E−N unit is the disappearance of the gauche conformation for φ_3 (Table 3) and in the case of the isotactic copolymer also a large decrease of the gauche content at φ_1, while the isotactic/syndiotactic difference at φ_2 (Table 5) is only slightly modified.

Table 6 shows that in all cases only one rotamer is present at the central N−N bond (φ_4), as already found for hydrodimers and dimethyl and diethyl dimers.[22] Here we find that the conformation of a N−N dyad embedded in an alternating E−N copolymer is remarkably similar to that of diethyl dimers. Indeed, Table 6 shows that gauche interactions in the N−N dyad are significantly different for the *M* and *R* configurations, independent of the tacticity of the adjacent N−E−N units.

Effect of N−N−N Triads. Here we limit the analysis to a couple of symmetric configurations. Addition of a third N unit further increases the rigidity of the adjacent (*meso*) N−E−N unit, substantially confined to the (*t t t*) state (see bottom lines of Tables 3 and 5). Even larger effects are found at the conformation at the central N−N bonds, which is drastically modified. Table 6 shows that in the *meso*/*meso* triad, dihedral φ_4 (and φ_5, by symmetry) has a significant gauche content, missing in the dyad (compare entry 6a with entries 5a and 5c): it arises from the presence of states *g*′− *t* and *t g*+ (Table 7), besides the major state *t t*, at dihedrals φ_4 and φ_5. In the case of *racemic*/*racemic* triad these two angles present two equivalent states *t*+ *g*+ and *g*′− *t*−, so that a population of nearly 50% of the (distorted) gauche conformer is calculated for φ_4, compared with 100% in the *racemic* dyad (compare entry 6b with 5b and 5d).

Ring Distortions. Norbornene ring distortions are represented by means of mainchain dihedrals ψ (rotations around bonds C2−C3) in Table 7. The calculations

Table 7. Conformations and Ring Distortions of the Lowest-Energy Minima of Several Model Compunds of E−N Copolymers[a]

met−N−E−N−E−N−met

confign	energy	ψ_1	φ_1	φ_2	φ_3	ψ_2	φ_4	φ_5	φ_6	ψ_3
mm	0.33	−2.1	−173.4	−179.0	174.8	0.0	−174.7	179.0	173.4	2.1
	1.07	−2.1	−171.8	−175.9	83.9	1.7	−173.2	178.0	172.3	2.4
rr	0.	−1.9	−174.6	172.7	−175.9	0.0	175.6	−173.1	174.4	1.9
	0.96	−1.7	−179.7	54.3	179.0	−0.1	174.6	−173.3	174.5	1.8

met−N−E−N−N−E−N−met

confign	energy	ψ_1	φ_1	φ_2	φ_3	ψ_2	φ_4	ψ_3	φ_5	φ_5	φ_6	ψ_7
mMm	3.23	−2.3	−173.1	−177.6	174.2	−14.1	180.0	14.1	−174.2	177.5	173.0	2.3
	4.26	−2.2	−173.1	−177.4	174.1	−14.0	180.0	14.0	−173.3	−179.6	80.7	4.0
rMr	2.90	−1.9	−175.2	169.8	−179.0	13.9	180.0	−13.9	179.0	−169.8	175.2	1.9
	3.66	−1.7	−179.8	53.0	175.3	14.1	179.5	−13.4	179.5	−169.3	175.5	1.9
mRm	0.	−2.3	−172.1	−177.2	171.2	−5.8	−73.3	−5.8	171.2	−177.2	−172.1	−2.4
	1.70	−3.9	−80.8	−178.5	169.4	−5.5	−72.6	−5.7	168.4	−176.4	−173.8	−1.8
rRr	0.41	−1.8	−174.5	173.1	−171.8	6.1	73.1	6.2	−171.4	173.8	−174.2	−1.8
	1.07	−1.9	−177.0	57.4	179.5	6.5	73.1	7.8	−170.8	176.3	−172.4	−2.1

met−N−E−N−N−N−E−N−met

confign	energy	ψ_1	φ_1	φ_2	φ_3	ψ_2	φ_4	ψ_3	φ_5	ψ_4	φ_6	φ_7	φ_8	ψ_5
mMMm	8.15	−2.1	−173.3	−179.1	171.3	−11.3	170.8	−28.1	−176.5	8.3	−175.2	176.9	173.0	2.5
	9.03	−2.1	−174.0	−177.1	176.2	−11.9	−73.1	26.3	−175.9	14.4	−170.9	179.4	173.5	2.2
mRRm	0.	−1.8	−172.5	−172.7	176.1	−13.3	−153.2	−4.8	77.1	5.5	−164.2	178.3	175.6	1.8
	1.15	−3.9	−80.5	−179.9	173.8	−14.3	−155.4	−4.9	77.4	5.8	−165.6	177.7	174.7	1.8
mMRr	1.99	−2.3	−173.1	−178.0	173.1	−13.4	177.5	3.6	−105.6	0.9	169.6	−175.1	174.0	1.9
	2.74	−2.3	−173.0	−177.9	173.5	−13.2	177.3	4.8	−108.2	−1.0	175.6	−61.3	176.4	2.1
mMRm	2.00	−2.3	−173.2	−178.4	172.8	−13.6	177.6	2.5	−103.7	2.2	167.4	−179.0	−173.7	−2.0
	2.97	−4.1	−80.5	179.4	173.0	−13.6	177.5	2.4	−103.5	2.4	167.2	−178.5	−173.6	−1.9

[a] In all stereoisomers the configuration of the first ring is *S/R*. Relative conformational energies are expressed in kcal/mol. The two most stable conformers are shown for each configuration.

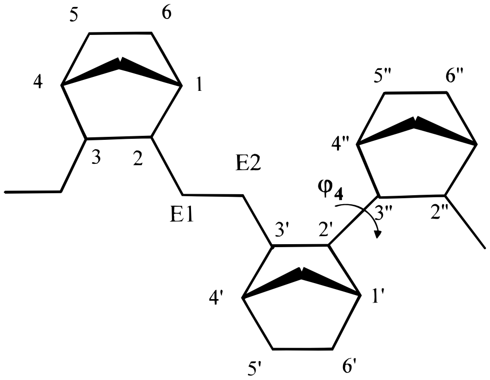

Figure 4. N−N dyad adjacent to a regular N−E−N unit.

show that while the ring keeps essentially unchanged its symmetrical structure when alternating with (or isolated in) ethylene units, large deformations are found for dyads and triads. Comparable variations are found for the dihedrals C7−C1−C2−C3′, while consistently smaller values are shown by the dihedrals C1−C2−C3−C4 and C4−C5−C6−C1. Also some bond angles are affected by changes of several degrees. The calculations show a much larger distortion for the *M* dyad, and an exceedingly large value of the central ψ for the *MM* triad; these distortions are related to the increasing conformational energy of adjacent meso norbornene sequences.

Influence of Conformation on the ^{13}C Chemical Shifts

1. Major Conformational Features of E−N Alternating Copolymers. The results presented in the previous section give a number of clear indications on the changes in conformer populations of the E−N chain, depending on tacticity and composition, which may affect the ^{13}C NMR spectra. Here we summarize such indications in terms of gauche content.

(a) The major difference between the two *perfectly alternating N−E copolymers* consists of a significantly larger population of the gauche conformer at the central E1−E2 bond in the syndiotactic copolymer, arising from the presence of the (*t g t*) state (see Figure 2b). A second (smaller) difference lies in a higher amount of conformer *t* at dihedrals φ_1 and φ_3 for the syndiotactic copolymer.

(b) The *alternating* units N−E−N keep their *meso*/*racemic* differences nearly unchanged when they are adjacent to E−E or N−N defects.

(c) In a defect N−E−E−N, the increased chain flexibility makes the average conformation at dihedrals φ_4, φ_5, and φ_6 nearly independent of the tacticities of the defect and of the copolymer. Moreover addition of a further ethylene unit leaves the gauche content at φ_4 and φ_5 almost unchanged. For these reasons one can practically expect a single signal (which we shall term *isolated*) for the norbornene carbons of this type of units.

(d) In defects N−E−E−..., there is a significantly lower gauche content at dihedral φ_5 than at φ_6: this difference is expected to produce appreciable ethylene signal splittings. However, the gauche content at further bonds is nearly constant and does not depend on tacticity: hence a rather limited number of ethylene signals is to be expected. (We note that *meso/racemic* population differences of the single conformers persist at φ_7 and further, but the total gauche content is nearly constant and independent from configuration from φ_6 on.)

(e) In −N−N− and −N−N−N− defects, it is found that different configurations correspond to large conformational differences, which are expected to produce strong effects on the chemical shifts. However, in these

Table 8. Comparison between the Major Estimated Stereochemical Effects ($\Delta\nu_{calcd}$) and the Corresponding Experimental Chemical Shifts (ν_{obs})[e]

	chemical shifts						contributions					
entry	carbon	ν_{obs}[b]	$\Delta\nu_{calcd}$	dihedral	$\langle\varphi\rangle$	$P_G{}^{\gamma}$	dihedral	$\langle\varphi\rangle$	$P_G{}^{\gamma}$	dihedral	$\langle\varphi\rangle$	$P_G{}^{\beta}$
1a	C2 isot	45.82	−0.55	φ_1	−82.0	0.184	φ_2	−70.1	0.052			
1b	C2 synd	45.21	−1.10	φ_1	−81.4	0.118	φ_2	54.5	0.172			
1c	C2 isolated	45.03	−1.23	φ_4	−83.3	0.132	φ_5	62.0	0.210			
2a	C1 isot[c]	40.04	−2.83	φ_1*	69.4	0.808						
2b	C1 synd	39.54	−3.05	φ_1*	66.8	0.874						
2c	C1 isolated	39.50	−3.01	φ_4*	67.3	0.861						
3a	$S_{\alpha\beta}$ isot[c]	28.74	−3.34	φ_1	−82.0	0.184	φ_1*	69.4	0.808	φ_2	−70.1	0.052
3b	$S_{\alpha\beta}$ synd	28.04	−3.76	φ_1	−81.4	0.118	φ_1*	66.8	0.874	φ_2	54.5	0.172
3c	$S_{\alpha\zeta}$ isolated	28.13	−3.84	φ_4	−83.3	0.132	φ_4*	67.3	0.861	φ_5	62.0	0.210
3d	$S_{\alpha\delta}$	28.20										
4a	$S_{\beta\gamma}$	28.41	−5.77	φ_4,[d] φ_4*	67.2	0.850	φ_5	62.0	0.221	φ_5, φ_6	63.2	0.559
4b	$S_{\beta\epsilon}$	27.95	−6.24	φ_4,[d] φ_4*	67.3	0.861	φ_7	63.6	0.317	φ_5, φ_6	63.2	0.551
5a	$S_{\gamma\delta}$	28.07	−4.24	φ_5	62.0	0.221	φ_7	63.6	0.317	φ_6, φ_7	63.8	0.647
5b	$S_{\delta\epsilon}$	27.80	−4.71	φ_6	64.0	0.330	φ_7	63.6	0.317	φ_7, φ_8	63.6	0.634

[a] From Table 1 of ref 16. [b] From Tables 1 and 2 of ref 22 and unpublished data from this laboratory. The ^{13}C NMR spectra were measured in $C_2D_2Cl_4$ at 105 °C; chemical shifts are referred to HMDS. [c] In copolymers with low N content the *isotactic* carbons C1 and $S_{\alpha\beta}$ present a second signal at 39.90 and 28.63 ppm, respectively, which can be assigned to *meso* alternating units next to −E−E− defects. See also ref 33. The present calculations appear inadequate to reproduce such fine effects, although Tables 3−5 show small changes in the conformer populations. [d] This contribution is not listed for brevity, but is included in $\Delta\nu_{calcd}$. [e] Carbons termed isot and synd refer to alternating N−E−N units. The γ and β contributions, derived from Tables 3−5, are listed besides each entry. $\Delta\nu_{calcd}$ values are tentatively estimated by assuming $\beta = -2.71$ ppm[a] and $\gamma = -5$, -4.62,[a] -3.5, and -2 ppm for values of $\varphi = 55$, 60, 70, and 80°, respectively.

cases even stronger effects arising from distortions of the norbornene rings may superpose to the pure conformational effects. Therefore, in this work, devoted to mainly alternating E−N copolymers, we do not attempt to quantify stereochemical shifts arising from NN dyads and triads.

2. Correlation between Conformational Changes and ^{13}C NMR Chemical Shifts. On the basis of the just described conformational changes, found in the chain of E−N copolymers as a function of tacticity and presence of chemical defects, we here try the first "conformational" interpretation of the observed ^{13}C NMR chemical shifts. This attempt relies on a method we have used in the past to interpret the chemical shifts of stereoirregular poly-α-olefins,[16,23] which consists of weighing specific conformational effects by means of the statistical analysis of the chain conformation. The most important of such effects is the well-known γ-gauche effect, which is a negative shift of about 4 ppm associated with a gauche conformation of the observed carbon with respect to an atom in γ position (the shift is relative to the signal of the same atom in the anti conformation).[24,25] For nonprimary carbons also a similar and smaller β-gauche effect, associated with the number of gauche conformations around the C−C bonds formed by the observed atom, is invoked.[16,23,26]

In principle, we define $P_G{}^{\gamma}$ (Cx) as the sum of the probabilities that a given carbon be in a gauche conformation with respect to its γ neighbors. (Similarly we may define $P_G{}^{\beta}$ (Cx) for the β-gauche effect). In these terms the chemical shift of atom Cx may be computed as

$$\nu(\mathrm{C}x) = \nu^0{}_{\mathrm{C}x} + \gamma P_G{}^{\gamma}(\mathrm{C}x) + \beta P_G{}^{\beta}(\mathrm{C}x) \qquad (2)$$

where $\nu^0{}_{\mathrm{C}x}$ is a constant representing the conformation-independent environment of atom type Cx (in terms of Lindeman and Adams' parameters α and β[27]) and γ and β represent the magnitude of the two effects.

To predict ν(Cx) we should also know γ and β, as well as $P_G{}^{\gamma}$ and $P_G{}^{\beta}$. In practice, since the magnitude of the γ effect decreases for growing values of φ, but we do not know the precise function $\gamma(\varphi)$, in Table 8, we list both the average dihedral value and the population of the various β and γ gauche contributions (derived from Tables 3−5). In many cases, we shall only discuss in terms of the contributions to $P_G{}^{\gamma}$. Nevertheless, in column 4 we try to quantify the stereochemical shifts on the basis of tentative assumptions.

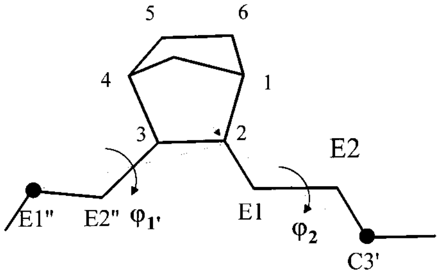

Figure 5. Conformation-dependent γ interactions for atom C2.

We expect that for norbornene polymers the ring deformations, that indeed we have found when NN dyads are present, or other ring effects, need to be taken into account. However, the proposed approach seems supported by the analysis of the assignment of the chemical shifts of hydro dimers and trimers due to Arndt et al.[9] Indeed, a comparison between the chemical shifts of the two dimer stereoisomers shows two major differences (of 2.1/2.3 ppm), which concern the only two carbons (C1, and C3) involved in conformation-dependent γ interactions. On the other hand the other atoms not involved in γ interactions present differences varying from 0.1 to 0.6 ppm.

Main-Chain Methine (Carbons C2/C3). In the regular (−E−N) sequence the variable γ interactions of atom C2, shown in Figure 5, are with carbon C3′ (depending on φ_2) and with E1″ (varying with dihedral E1″−E2″−C3−C2); the latter interaction is equivalent to that of atom C3 with E2, which is a function of φ_1.

The top lines of Table 5 show that the sum of the contributions of the two conformers to the first interaction is 0.17 for the syndiotactic copolymer, with a $\langle\varphi_2\rangle$ value of 54°, while in the isotactic case the sum amounts only to 0.05, with a much larger $\langle\varphi_2\rangle$ (70°). The second gauche interaction is always quite distorted: Table 8 indicates a significantly higher population in the isotactic case (0.184 vs 0.118, with a $\langle\varphi_1\rangle$ value of −82°). Thus, the stereochemical shifts of the mainchain *methine* in the two *regularly alternating* E−N copolymers are determined by two contrasting effects, but the strong interaction C2···C3′ in the syndiotactic copolymer is clearly prevailing, so that an upfield $\Delta\nu_{\mathrm{calcd}}$ of ∼−0.5 ppm with respect to the isotactic signal is estimated.

The environment of the C2/C3 methine in an *isolated* N unit may be approximated to that in $(\mathrm{N-E-E-E})_x$. The γ contribution for this methine reported in Table 8 (item 1c, derived from Table 4, for φ_4, and Table 5, for φ_5) indicates a small increase of the populations with respect to the regular syndiotactic copolymer, but also a larger $\langle\varphi_5\rangle$ for the most important conformer (62 vs 54°). Thus, the signal of this *methine* should fall close to the syndiotactic signal, and it is certainly upfield relative to the signal of the regular isotactic methine.

As shown above, the E−E− defects little affect the gauche content of the N−E−N adjacent unit. Here we only point out that at the N−E−E norbornene unit, while C3′ (Figure 3) keeps nearly unchanged the syndio/isotactic difference, the C2′ methine shows no such difference at all and is only slightly affected by the *meso/racemic* configuration of the defect: all signals of this C2′ should fall close to the isolated N methine signal.

Ring Methine (Carbons C1/C4). In the regularly alternating copolymers the chemical shift of this methine should depend on the gauche content of dihedral φ_1* (C1−C2−E1−E2). Table 8 (entries 2a−c) shows a small increase (0.07) in $P_G{}^{\gamma}$ (C1) of the syndiotactic copolymer with respect to the isotactic one; hence, a small upfield shift of the syndiotactic signal is estimated, while the signal of the C1 of an isolated N unit should be very close to the syndiotactic value.

Ethylene CH$_2$. Due to intrinsic differences in ν^0 and to possible distortion effects deriving from the proximity of the N ring, we cannot order the relative shifts of various ethylene carbons. However, use of the populations of Tables 3−5 leads to the prediction of three significant chemical shift differences between *homogeneous atoms*. Such shifts arise essentially from two, already discussed, properties of the copolymer chain: (a) the *meso/racemic* conformational difference in the N−E−N unit; (b) the lower gauche content for φ_5 with respect to dihedrals farther from N.

In Table 8 (entries 3a−c) an upfield shift of the signal of carbon E2 in the regular syndiotactic N−E−N unit (indicated as $S_{\alpha\beta}$ in Figure 6) is predicted with respect to the isotactic copolymer, since in the former copolymer there is a larger population of the less distorted gauche φ_1 conformer, and a larger $P_G{}^{\beta}$ (E2) (function of φ_2).

In addition, the relative position of the E11 signal (alias $S_{\alpha\delta} \cong S_{\alpha\zeta}$) at a N−E−E−N defect (see Figure 6), depends on the mentioned different strength of γ-gauche effect ($P_G{}^{\gamma} \cong 0.35$ at φ_6), while $P_G{}^{\beta}$ at φ_5 is close to the value for E1/syndio; thus this signal is estimated to be close to the syndio-$S_{\alpha\beta}$ signal.

Finally, considering the β carbons a downfield shift of about 0.5 ppm is expected for E12 in N−E−E−N (i.e., $S_{\beta\gamma}$) with respect to the same carbon in N−E−E−E− (i.e., $S_{\beta\epsilon}$; see Figure 7), owing to a difference of −0.1 in $P_G{}^{\gamma}$. The same shift is expected for the signal of E21 (i.e., $S_{\gamma\delta}$) with respect to $S_{\delta\epsilon}$, which is very close to the polyethylene signal.

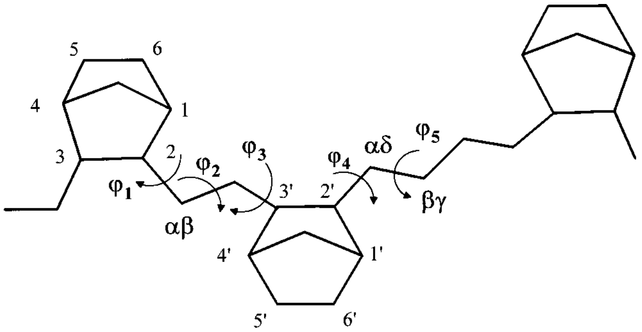

Figure 6. Segment N−E−N−E−E−N, showing the usual notation whereby two greek subscripts indicate the distance of a secondary carbon S from the left and right methines (letter S here being omitted for simplicity).

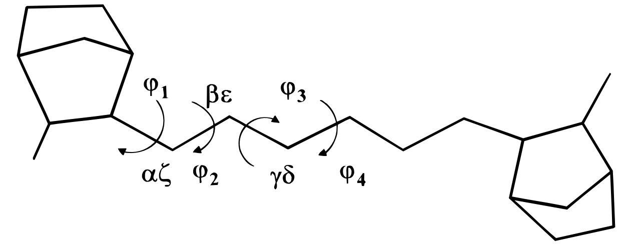

Figure 7. Segment N−E−E−E−N, showing the dihedral angles affecting the shifts of the different ethylene carbons.

3. ^{13}C NMR Spectra of Alternating Stereoregular and Stereoirregular E−N Alternating Copolymers. The stereochemical shifts predicted for ethylene carbons and norbornene C1 and C2 carbons of *meso*, *racemic*, and isolated units of the copolymer chain prompted us to carry out a more attentive analysis of the ^{13}C NMR spectra and of the data reported in the literature.[7b,9−12,22] In fact, due to the complexity of the spectra, despite numerous recent investigations of the copolymer microstructure by ^{13}C NMR, the chemical shift assignments are still limited. Even when confining our attention to the alternating ethylene−norbornene copolymers, there exist inconsistencies concerning the assignments of some atoms and peak intensities.[7b,22,28] In the literature there are several examples of mainly alternating copolymers, prepared with C_1-symmetric bridged metallocenes or with half-metallocenes. Some of these copolymers are considered stereoregular alternating copolymers on the basis of the simplicity of the spectra and of their crystallinity: however, no mention[29] can be found of the isotactic or syndiotactic type of regularity.

We ourselves, in the initial analysis of the spectra, were not aware of possible stereochemical effects on the chemical shifts of alternating $(\mathrm{NE})_x$ copolymers; although we have recently assigned as isotactic a highly stereoregular and mainly alternating copolymer,[22] for which we found it necessary to exchange the previous assignments of the ethylene and norbornene methylenes. A deeper inspection of the ^{13}C NMR spectra of ethylene−norbornene copolymers prepared with the C_s-symmetric $\mathrm{Me_2C(Flu)(Cp)ZrCl_2}$ metallocene allowed us to notice either the broadening of the signals of carbons of isolated norbornene units or the presence of signals which could be ascribed to *syndiotactic alternating* units. We suspected that the vicinity of the chemical shifts of

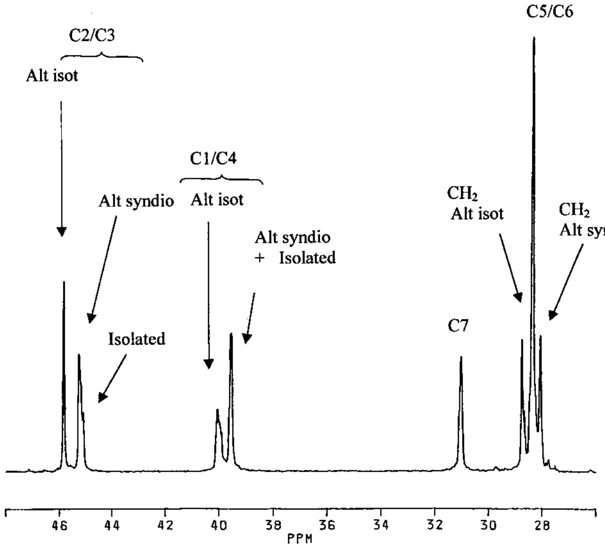

Figure 8. ^{13}C NMR spectrum of the ethylene−norbornene copolymer prepared with $Me_2Si[(Me_4Cp)N^tBu]TiCl_2$ and MAO catalyst. The spectrum was measured in $C_2D_2Cl_4$ at 105 °C, chemical shifts are referred to HMDS.

the syndiotactic alternating units and of the isolated units is the reason for the total absence of the former in the literature. Moreover, ethylene−norbornene copolymers which contain at least 35 mol % of norbornene, prepared with asymmetric metallocenes or with half-metallocenes, sometimes are credited with a percentage of isolated EENEE sequences which seemed to us exceedingly high. The case of the spectra of E−N copolymers prepared with $Me_2Si[(Me_4Cp)N^tBu]TiCl_2$ and with $^iPr(3\text{-}^iProp\text{−}Cp)FluZrCl_2$, having approximately the same norbornene content (41.9 and 43.2 mol %, respectively),[7b] seemed the most interesting to us. Since syndiotactic alternating sequences had not been identified, the authors had to conclude, with some stoichiometric inconsistency: "Although both copolymers are nearly of the same norbornene content there are more isolated norbornene units than alternating sequences in the copolymer produced by the half-sandwich catalyst."[7b]

This prompted us to prepare an ethylene−norbornene copolymer with the same $Me_2Si[(Me_4Cp)N^tBu]TiCl_2$ catalyst and with a similar norbornene content and to perform the ^{13}C NMR analysis of the sample under the same conditions—solvent and temperature—as for the copolymers earlier prepared[30] with $Me_2C(Flu)(Cp)ZrCl_2$, *rac*-$Me_2Si(Ind)_2ZrCl_2$, and *rac*-Me_2Si(2-Me-[*e*]benzindenyl)$_2ZrCl_2$ catalysts. The spectrum of the sample is reported in Figure 8.

Comparison of comparable chemical shifts confirmed our working hypothesis and allowed us to make the assignments reported in the third column of Table 8. Such assignments correspond to a qualitative agreement between observed and calculated stereochemical shifts for the three carbons C1, C2, and $S_{\alpha\beta}$, and also appear to rationalize previously unexplained peak intensities (see, for example, parts A′, B′, and C′ Figure 2 of ref 22).

Having cleared the shifts of the above carbons, we could reexamine the complete spectra of a series of ethylene−norbornene copolymers prepared with the previously mentioned catalysts, with norbornene content ranging from 20 to 40%, where the alternating sequences are visible. The region of the spectra containing the ethylene secondary carbons reveals two signals with the same intensity, at 28.41 and 28.20 ppm, associated with the probability of presence of NEEN sequences, and thus assignable to carbons $S_{\beta\gamma}$ and $S_{\alpha\delta}$ (see Figure 6). A second group of signals at 28.13, 28.07, and 27.95 ppm are quite visible as well, their related intensities increasing with the probability of NEEEN sequences, so that they can be attributed (in some order) to carbons $S_{\alpha\zeta}$, $S_{\beta\epsilon}$, and $S_{\gamma\delta}$ (see Figure 7). Finally, the signal at 27.80 ppm, close to the polyethylene signal, can be assigned to $S_{\delta\epsilon}$. The conformational calculations indicated that the chemical shifts of $S_{\alpha\delta}$ and $S_{\alpha\zeta}$ should not differ significantly, while a significant downfield shift is expected for carbon $S_{\beta\gamma}$ of NEEN relative to $S_{\beta\epsilon}$ of NEEE−. Hence the signal of $S_{\beta\gamma}$ should fall well downfield with respect to the group of NEEEN signals, and we assigned the chemical shifts at 28.41, 28.20, and 28.13 ppm to carbons $S_{\beta\gamma}$, $S_{\alpha\delta}$, and $S_{\alpha\zeta}$, respectively. Similarly, the calculation predicts a downfield shift for carbon $S_{\gamma\delta}$ with respect to $S_{\delta\epsilon}$: such a difference is best fitted by assigning the signals at 28.07 and 27.95 pmm to carbons $S_{\gamma\delta}$ and $S_{\beta\epsilon}$, respectively, but the alternative choice cannot be ruled out. Although the $\Delta\nu_{obs}$ between $S_{\beta\gamma}$ and $S_{\beta\epsilon}$ and between $S_{\gamma\delta}$ and $S_{\delta\epsilon}$ are somewhat smaller than $\Delta\nu_{calcd}$, these estimates, combined with the experimental data (chemical shifts and peak intensities), have made possible a complete assignnment of ethylene CH_2 region of the spectrum.

Ring CH_2 (Carbons C5/C6). In our computational scheme, the chemical shifts of these carbons are not affected by conformation-dependent effects. Accordingly, essentially a unique signal is observed for C5/C6 in all copolymers presenting only isolated or alternating norbornene units. On the contrary, Bergström et al.[10] have proved that a very large splitting between the signals of the C5 and C6 atoms of the same ring occurs in the presence of N−N dyads. As in other cases, the assignment of the hydro dimers and trimers by Arndt et al.[9] is very precious. Indeed, the chemical shift of the CH_2 "internal" to the dyad[10] is very close to the value assigned to the central C5/C6 carbons of the *mm* hydrotrimer (and to C5 in the *mr* hydrotrimer). On the other hand, in high norbornene-content copolymers prepared with $Me_2C(Flu)(Cp)ZrCl_2$ and containing *racemic* NEN sequences, Tritto et al.[22] found that the signal of the dyad "internal" CH_2 coincides with the one assigned to the central C5/C6 carbons of the *rr* hydrotrimer (and to C6 in the *mr* hydrotrimer).[9] Thus, it appears that the chemical shift of the internal CH_2 depends mainly on the dyad configuration, while on the other side the presence of another norbornene (in the hydrotrimers) is nearly equivalent to that of the ethylene of the copolymer chain. The chemical shifts of the "external" CH_2's are similar to those of the C5a/C5b carbons of the hydrotrimers, but not quite equal, as here the chain in position γ is missing.

In our opinion, such large shifts can be interpreted in terms of ring distortions. We have already shown (Table 7) that significant deformations of the norbornene rings of the copolymer chain arise only in the presence of N−N dyads and triads, and they are much stronger when the configuration of the dyad is *meso*. Moreover, such distortions are similar to those previously computed for alkyl dimers and hydrotrimers. These results correlate qualitatively with the stereochemical shifts found by Arndt and with the recent assignments of the C5/C6 signals.

Also the difference between the *meso* and *racemic* signals of carbons C2/C3 internal to a dyad N−N originates from the ring distortions, as pointed out earlier.[22] In other cases, such effects superpose to conformational differences, hindering at the moment a more general understanding of stereochemical shifts due to N−N dyads and triads.

Conclusions

We have presented a statistical treatment of the alternating ethylene−norbornene copolymer chain, based on the results of MM3 calculations with inclusion of the solvent term. The E−N chain turns out to be rather rigid, only few conformers contributing to the average structure. The major feature of the chain is that the N−E−N unit presents two distinct conformational patterns depending on the *meso/racemic* configuration of the unit; such distinction is maintained also when E−E or N−N defects are adjacent to the alternating unit.

This result leads to the prediction of distinct ^{13}C NMR signals, respectively, for the isotactic and the syndiotactic regularly alternating copolymers, of the ring methines, and of the ethylene CH_2, the syndiotactic signal occurring *upfield* for all three carbons. Such a distinction had not been evidenced in the literature so far and accounts for the available experimental data.

A second result is that for a norbornene inserted in long ethylene sequences, the conformational environment of the ring methynes (and also of the CH_2 in position α) is similar to that of the syndiotactic alternating copolymer, so that the signals occur upfield with respect to the isotactic signals. This is in agreement with previous assignments of the observed spectra. Indeed, the iso/syndio difference was masked by the proximity of syndiotactic and isolated signals.

Significant conformational effects concerning other ethylene carbons are also suggested by the calculations and turn out to be confirmed by experiment. These results allowed us to achieve a complete and unambiguous assignment of the spectra of mainly alternating stereoregular and irregular E−N copolymers.

Finally, specific large conformational (configuration-dependent) changes are found for N−N dyads and triads; however, these changes are associated with strong ring distortions (particularly in the case of *meso* dyads), whose effects on the chemical shifts are beyond the scope of the present treatment. Hence, further work is required to complete the interpretation of the spectra of E−N copolymers with high norbornene content. Hopefully, a priori quantum-mechanical chemical shift computations[31,32] may help clarify this point. Nevertheless, by combining the available assignments with the indications on the ring distortion effects and with the consistency between peak areas and stoichiometric requirements, it is possible to pursue further the assignment of the ^{13}C NMR spectra of ethylene−norbornene copolymers which contain NN sequences, as we shall report elsewhere.

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