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Ethylene−Norbornene Copolymer Microstructure. Assessment and Advances Based on Assignments of ^{13}C NMR Spectra[†]

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ABSTRACT: A best-fitting procedure for the quantitative determination of the molar fractions of the stereosequences that define the microstructure of an ethylene−norbornene (E−N) copolymer from ^{13}C NMR spectra has been set up. The quantitative determination of copolymer microstructure will allow one to clarify the E−N copolymerization mechanism. This method utilizes the observed peak areas of the ^{13}C signals and takes into account the consistency between peak areas and the stoichiometry of the copolymer chain. Thus, a further extension of signal assignments is made possible by guessing assignments of unknown signals and by discarding inconsistent hypotheses. This procedure has been applied to the analysis of the ^{13}C NMR spectra of a large number of E−N copolymers, prepared with catalyst precursors *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**), *rac*-Me$_2$Si(2-Me-benz[*e*]indenyl)$_2$ZrCl$_2$ (**2**), Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**3**), and Me$_2$C(Flu)(Cp)ZrCl$_2$ (**4**). An estimate of the molar fractions of the various stereosequences with a standard deviation on the order of 1−2% has been obtained. The comparison between controversial assignments existing in the literature for a number of ethylene signals has confirmed our previous assignments. New signals such as those of the C2/C3 carbons of EENNEE *meso* sequences (*M*) and of the external carbons C5 of *MM* and *MR* triads in ENNNE sequences have been assigned.

Introduction

The discovery of metallocene−methylaluminoxane-based catalysts has caused an upsurge of academic and industrial research in the field of transition-metal-catalyzed olefin polymerization.[1] The exploitation of changes in metallocene symmetry and ligands yielded catalysts with increased selectivity, stability, or productivity with respect to the first racemic ansa-bridged metallocene obtained by Brintzinger.[2] Among the advances produced by these catalysts are the syntheses of new classes of polymers such as ethylene−norbornene (E−N) copolymers.[3−5] The resulting amorphous E−N copolymers are of great interest because of their transparency, high glass transition temperatures, and good heat resistance. They can be used in optical applications such as coatings for compact disks. Although their first synthesis was already reported in 1991,[3] the structure of these copolymers has not yet been thoroughly investigated.

^{13}C NMR spectroscopy is surely the most powerful method for polymer microstructural investigations. However, E−N copolymer spectra are quite complex for the presence in the polymer chain of two stereogenic carbons per norbornene unit and for the fact that the chemical shifts of these copolymers do not obey straightforward additive rules, owing to the bicyclic nature of the norbornene structural units. Thus, until recently analyses of ^{13}C NMR spectra were scarce, and only in the past few years have a number of groups accepted the challenge of assigning the ^{13}C NMR spectra of E−N copolymers.[6−15]

Our group has devoted a significant effort to clarifying some of the shifts in the ^{13}C NMR spectra of E−N copolymers, especially taking into account *meso/racemic* relationships between norbornene units in alternating NEN and in ENNE sequences, i.e., accounting for the configuration, as well as for the composition, of the copolymer chain.[10,12−15]

At the onset of our studies, no mention of *isotactic* or *syndiotactic* types of regularity for alternating NENEN or of *meso/racemic* norbornene diads (ENNE sequences) had been found in the literature. Our investigations were based on the comparison of ^{13}C NMR spectra of E−N copolymers of various compositions prepared with different metallocenes. Substantial progress has come from the elucidation of the conformational structure of the chain of E−N copolymers on the basis of molecular mechanics calculations and from the correlation between conformation and ^{13}C NMR chemical shifts.[15,16] A comparison of conformer populations for stereoregular and stereoirregular alternating E−N copolymer chains predicted stereochemical shifts in these copolymers and allowed us to recognize and distinguish isotactic and syndiotactic N−E−N sequences. Conformer modeling evidenced strong deformations of the norbornene rings in N−N diads or triads and allowed us to understand the splitting of C5/C6 signals, such distortions being much stronger in *meso* diads. INADEQUATE ^{13}C−^{13}C correlated NMR spectra were also of great help in correcting previous assignments of ethylene and norbornene methylenes.[9,13]

Quantitative analysis of copolymer sequences is needed for determining the sequence distribution at the triad level or higher, which allows one to understand the copolymerization mechanism. In the present work we have examined the complete ^{13}C NMR spectra of a great number of E−N copolymers, prepared with different catalysts and having various norbornene contents.

Starting from the available certain assignments and taking into account the consistency between peak areas and the stoichiometric requirements of the copolymer chain, we have set up a procedure for the determination

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[†] Dedicated to Prof. Umberto Giannini on his 70th birthday.

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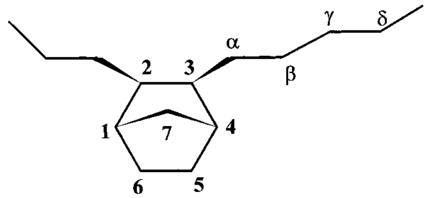


Figure 1. Isolated −E−N−E−E− segment of an ethylene−norbornene chain showing carbon atoms numbering.

of the different stereosequences of E−N copolymers. This method can be used to guess assignments of unknown signals and to verify the new signal assignments by discarding inconsistent hypotheses, allowing one to further extend signal assignments. As these studies were completed, other ^{13}C NMR studies of E−N copolymer microstructures were reported,[17−19] showing that a disagreement in the interpretation of a number of signals exists in the literature. Thus, the procedure has also been used to compare the different existing assignments, and the results will be discussed. The complete assignments of the spectra of E−N copolymers containing ENNE diads will be reported.

As a result of this analysis, we shall point out that some norbornene signals in ENNE sequences and the central ethylene signals in EN*E*NE are sensitive to the type of adjacent comonomer sequences. Furthermore, although the triad assignments have not been pursued in detail, the methodology reported allows us to quantify the norbornene present in norbornene triads (NNN) or longer sequences.

Ethylene−Norbornene Copolymer Microstructure and Previous ^{13}C NMR Assignments. Previous studies have shown that norbornene in metallocene-catalyzed copolymerization is enchained by 2,3-*exo*-cis addition.[3] A section of an ethylene−norbornene chain (EENEE) in which norbornene can be considered isolated from other norbornene units is shown in Figure 1 along with the numbering of carbon atoms used. Figure 2 gives an overview of possible segments of an E−N copolymer chain in which norbornene units are in alternating (ENENE), diad (ENNE), and triad (ENNNE) sequences, without considering stereochemical differences. The adopted numbering of norbornene carbons, which is similar to that of other authors,[19] has been chosen in order to evidence differences in assignments; thus, C2, C1, and C6 are always closer to another norbornene unit than atoms C3, C4, and C5, respectively. Moreover, configuration at atoms C2/C3 in a ring can be either *S*/*R* or *R*/*S*, and the relationship between two subsequent norbornene units can be either erythro di-isotactic (*meso*) or erythro di-syndiotactic (*racemic*). The possible stereochemical environments of norbornene in alternating sequences, diads, and triads are illustrated in Figure 3. Our previous findings have shown that erythro di-isotactic and erythro di-syndiotactic microstructures of E−N−E−N−E and E−N−N−E segments can be obtained depending on the catalyst structure.[12−15]

The spectrum of an E−N copolymer with 50.8 mol % of norbornene produced by catalyst *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**) is shown in Figure 4. General assignments of norbornene and ethylene carbons allow us to calculate the mole percent of norbornene incorporated in the polymer. At a higher level of norbornene the spectra are more complex since the various stereosequences of triads and longer norbornene sequences originate splittings and shifts of the signals, which can make even the norbornene content uncertain.

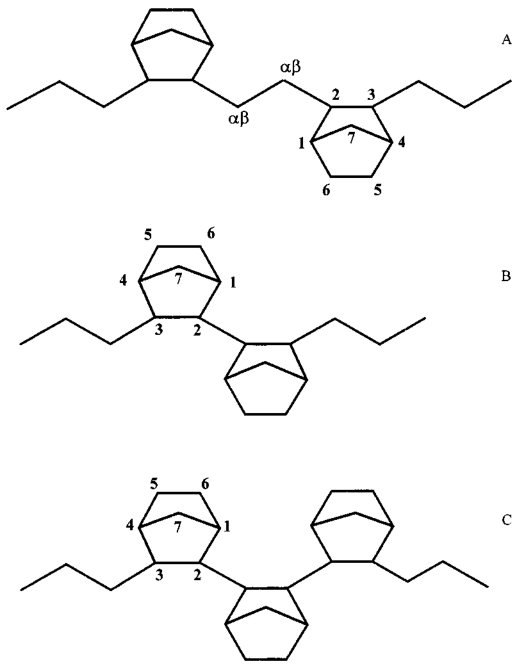


Figure 2. Overview of possible segments of an E−N copolymer chain where norbornene units are in alternating (ENENE), diad (ENNE), and triad (ENNNE) sequences.

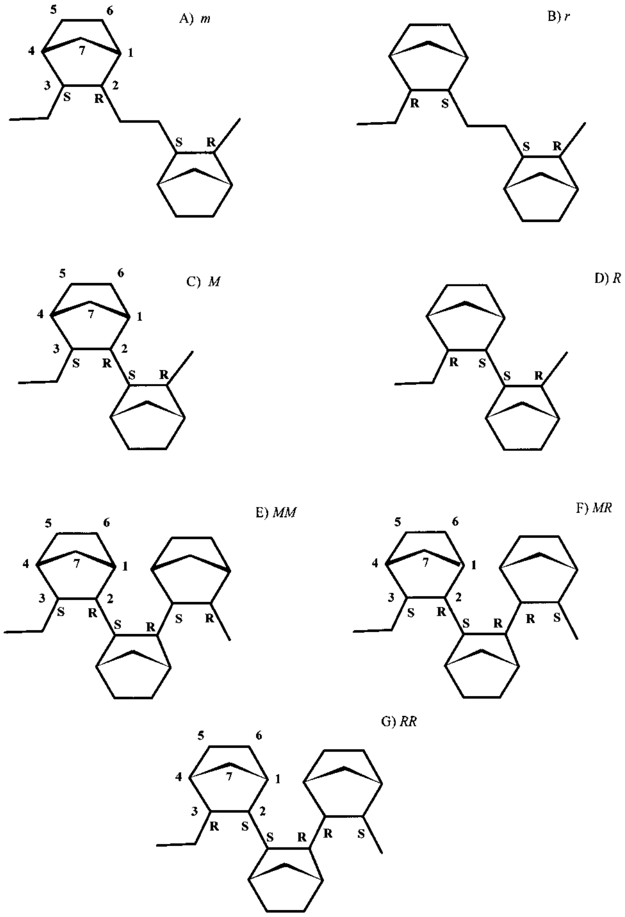


Figure 3. Erythro di-isotactic (*meso*) and erythro di-syndiotactic (*racemic*) stereochemical environments of norbornene in alternating sequences (A and B), diads (C and D), and triads (E−G).

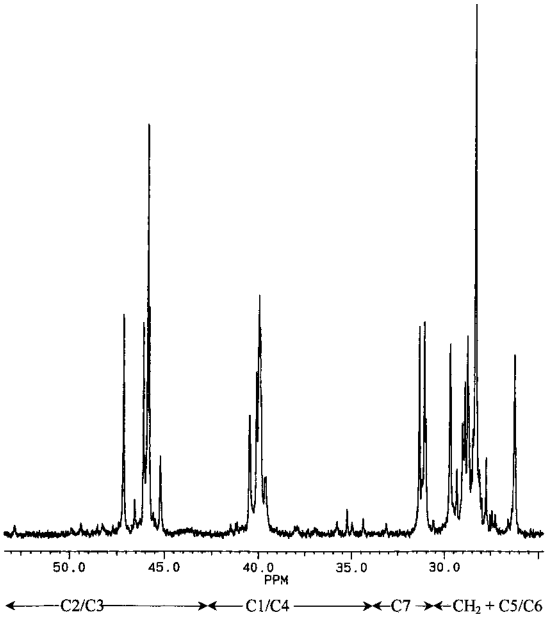


Figure 4. ^{13}C NMR spectrum of an E–N copolymer with 50.8 mol % of norbornene produced by catalyst *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**).

Our previous assignments of ^{13}C NMR spectra of E–N copolymers[10,12–15] are summarized in Table 1. The region of tertiary carbons C2/C3 between 45 and 55 ppm and the region of C5/C6 and of the methylenes of ethylene units are the most sensitive to differences in microstructural environments and hence are the ones that have been analyzed in greater detail for different sequences. Besides the above assignments published earlier, Table 1 also includes further assignments of C1/C4 and C7 signals corresponding to the same sequences. These assignments could be easily obtained by analyzing the complete spectra of copolymers with different norbornene content and by comparing the relative peak areas. Several of these assignments are in agreement with those reported by other authors.[7,9,18,19] A specific comparison of controversial assignments will be presented in one of the following sections.

Examples of spectra of E–N copolymers prepared with four different catalyst precursors are presented in order to evidence signal assignments of stereoregular and stereoirregular alternating E–N copolymers, as well as the assignments of the most relevant carbons in ENNE *meso* and *racemic* sequences reported in Table 1. This will evidence the complexity of the spectra we are dealing with and will make clear the procedure used in the following sections to extend the assignments. A more in-depth discussion of relationships between catalyst ligand, polymer structures, and polymer properties will be reported elsewhere.

The ^{13}C NMR spectra of E–N copolymers produced with *rac*-Me$_2$Si(2-Me-benzindenyl)$_2$ZrCl$_2$ (*KM103*) (**2**) and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (*KM108*) (**3**) based catalysts are compared in Figure 5, A and B, respectively. The two copolymers contain 43.6 and 43.5 mol % of norbornene. The spectra are relatively simple due to the mainly alternating nature of these copolymers. The main differences in the more intense signals are due to the isotactic or syndiotactic type of stereoregularity in the copolymers prepared with catalyst **2** and **3**, respectively.

In Figure 6 the spectra of E–N copolymers prepared with *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**) with increasing norbornene content are compared. This catalyst precursor having C_2 symmetry produces mainly *meso* stereoresequences, and the C2/C3 signals at 47.12 and 46.04 ppm characteristic of *meso* ENNE diads become more intense as the norbornene content increases.

Table 1. Assignments of ^{13}C Chemical Shifts (ppm) for Carbons of Norbornene and Ethylene Units in E–N Copolymers

sequence type[a]	config	carbon	chemical shifts[b]	sequences	ref
			Ethylene[c]		
I	$S_{\delta+\delta+}$	CH_2	27.73	EEE*E*EEE	10
I	$S_{\delta\delta+}$	CH_2	27.80	NE*E*EEE	10
I	$S_{\beta\delta+}$	CH_2	27.95	N*E*EEE	15
A	$S_{\alpha\beta}$ synd	CH_2	28.04	EN*E*NE	15
I	$S_{\gamma\delta}$, $S_{\gamma\delta+}$	CH_2	28.07	NE*E*E	15
I	$S_{\alpha\delta+}$	CH_2	28.13	N*E*EE...	13
I	$S_{\alpha\delta}$	CH_2	28.20	NEEN	13
I	$S_{\beta\gamma}$	CH_2	28.41	NEEN	15
A	$S_{\alpha\beta}$ isot	CH_2	28.63	EEN*E*NEE	15
A	$S_{\alpha\beta}$ isot	CH_2	28.74	NEN*E*NEN	15
			Norbornene		
D	isot	C5	26.24	ENNE	12, 13, 14
D	synd	C5	27.58	ENNE	12, 13, 14
I		C5/C6	28.33	EE*N*EE	12, 13, 14
A	synd	C5/C6	28.33	NE*N*EN	12, 13, 14
A	isot	C5/C6	28.33	NE*N*EN	12, 13, 14
D	synd	C6	29.37	ENNE	12, 13, 14
D	isot	C6	29.68	ENNE	12, 13, 14
I		C7	30.90	EE*N*EE	10
A	isot	C7	30.98	NE*N*EN	this work
A	synd	C7	30.98	NE*N*EN	this work
A	isot	C7	31.05	NE*N*EN	this work
D	isot	C7	31.17	ENNE	this work
D	isot	C7	31.32	ENNE	this work
D	synd	C7	31.57	ENNE	this work
D	synd	C1	38.93	ENNE	this work
I		C1/C4	39.50	EE*N*EE	10
A	synd	C1/C4	39.54	NE*N*EN	15
D	isot	C1	39.88	ENNE	this work
A	isot	C4	39.90	EE*N*EN	15
A	isot	C1	40.04	NE*N*EN	15
D	isot	C4	40.43	ENNE	this work
I		C2/C3	45.03	EE*N*EE	10
I		C3	“	EE*N*EN	
A	synd	C2	45.21	NE*N*EN	15
D	synd	C3	45.62	ENNE	12, 13, 14
A	isot	C2	45.82	NE*N*EN	12, 13, 14
D	isot	C3	46.04	ENNE	12, 13, 14
D	isot	C2	47.12	ENNE	12, 13, 14
D	synd	C2	48.07	ENNE	12, 13, 14

[a] Sequence key: I, isolated; A, alternative; D, NN dyad; isot, isotactic; synd, syndiotactic. [b] The ^{13}C NMR spectra were measured in $C_2D_2Cl_4$ at 105 °C; chemical shifts are referred to HMDS. [c] The Greek subscripts indicate the distance of the observed secondary carbon atom S from the closest norbornene carbons[10] (see also Figures 2 and 9).

The C_s symmetric Me$_2$C(Flu)CpZrCl$_2$ (**4**) based catalyst shows a high selectivity for producing E–N copolymers with *racemic* ENNE diads. In Figure 7, where the spectra of copolymers obtained by catalyst precursor **4** are compared, the intensity of the C2/C3 signals at 48.07 and 45.62 ppm, characteristic of *racemic* ENNE sequences, clearly increases with the norbornene content.

In Figures 5A and 6C a number of small signals in all the regions appear which are due to the norbornene blocks longer than diads. Their large number is due to the increase of possible stereosequences with the increase of norbornene block length. However, detailed assignments of such signals to the specific configuration of C2/C3 carbons of norbornene triads are not available.

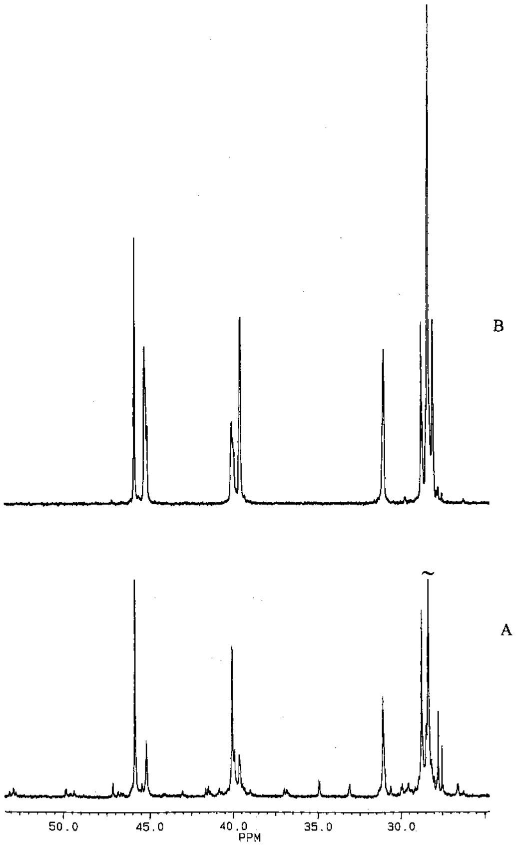


Figure 5. ^{13}C NMR spectra of copolymer samples *KM103* (A) prepared with *rac*-Me_2Si(2-Me-benz[*e*]indenyl)$_2ZrCl_2$ (**2**) and *KM108* (B) prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**3**).

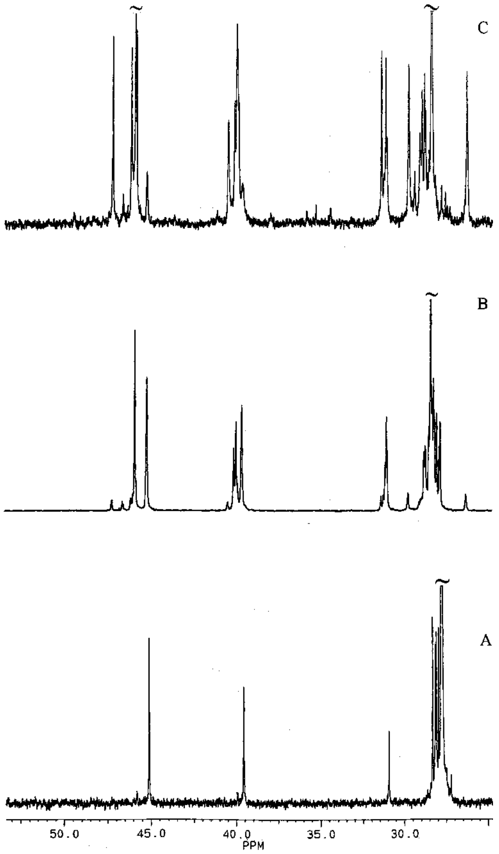


Figure 6. ^{13}C NMR spectra of E−N copolymers prepared with *rac*-Et(indenyl)$_2ZrCl_2$ (**1**), with N mole percent: 4% (A); 33% (B); 52% (C).

Method

To obtain a quantitative determination of the different stereosequences of E−N copolymers from the observed integrals of signals of ^{13}C NMR spectra and to extend previous assignments, we have set up a procedure starting from assignments of the different peaks already available. The E−N copolymer chain sketched below (Figure 8) has a typical random copolymer sequence distribution and is composed of the segments listed in Figure 2. It should be noted that such a classification of the segments does not correspond to the complete sequence assignment at a given level (e.g., at pentad level), but rather it is adequate to the present state of the interpretation of the ^{13}C NMR spectra in terms of sequence composition. Indeed, the current assignments of the ethylene CH_2 signals are much more detailed than those for the signals arising from norbornene carbons. The classification is obviously open to further extensions as the interpretation of the spectra will improve.

Our purpose is to determine the molar fractions of *isolated*, *alternating* sequences, NN *diads* and *blocks* (triads and longer sequences), and to distinguish between *meso* and *racemic* alternating or diad sequences. The analysis of the spectra provides a certain number of peak integrals, each peak corresponding to one or more signals. For each peak we can write a linear equation describing the observed (normalized) integral as a function of the unknown molar fractions. A further equation is provided by the average observed norbornene content. We obtain a set of linear equations, whose variables are chosen among the molar fractions defined below. A number of stoichiometric constraints reduce the number of independent variables. Least-squares fitting of the (weighted) set of equations provides the best solution for the unknown molar fractions.

Definitions of Molar Fractions. The E and N molar fractions are obviously

$$f(\mathrm{N}) = \frac{[\mathrm{N}]}{[\mathrm{N}] + [\mathrm{E}]} \qquad f(\mathrm{E}) = \frac{[\mathrm{E}]}{[\mathrm{N}] + [\mathrm{E}]} \tag{1}$$

where

$$f(\mathrm{N}) + f(\mathrm{E}) = 1 \tag{2}$$

The molar fractions of alternating, isolated, diad and block sequences are defined as following, where we distinguish between *meso* and *racemic* alternating sequences ($f(m)$ and $f(r)$, respectively) and between *Meso* and *Racemic* diads ($f(M)$ and $f(R)$, respectively):

$$f(\mathrm{alt}) = [\mathrm{N{-}E{-}N}]/\{[\mathrm{N}] + [\mathrm{E}]\} = f(m) + f(r) \tag{3}$$

$$f(\mathrm{isl}) = \{\sum_{i=0}[\mathrm{N{-}E{-}E}_i\mathrm{{-}E{-}N}]\}/\{[\mathrm{N}] + [\mathrm{E}]\} = \sum_{i=0} f_i \tag{4}$$

$$f(\mathrm{diad}) = [\mathrm{E{-}N{-}N{-}E}]/\{[\mathrm{N}] + [\mathrm{E}]\} = f(M) + f(R) \tag{5}$$

$$f(\mathrm{block}) = \{\sum_{i=1}[\mathrm{E{-}N{-}N}_i\mathrm{{-}N{-}E}]\}/\{[\mathrm{N}] + [\mathrm{E}]\} = f(\mathrm{triad}) + ... \tag{6}$$

The total E content is given by

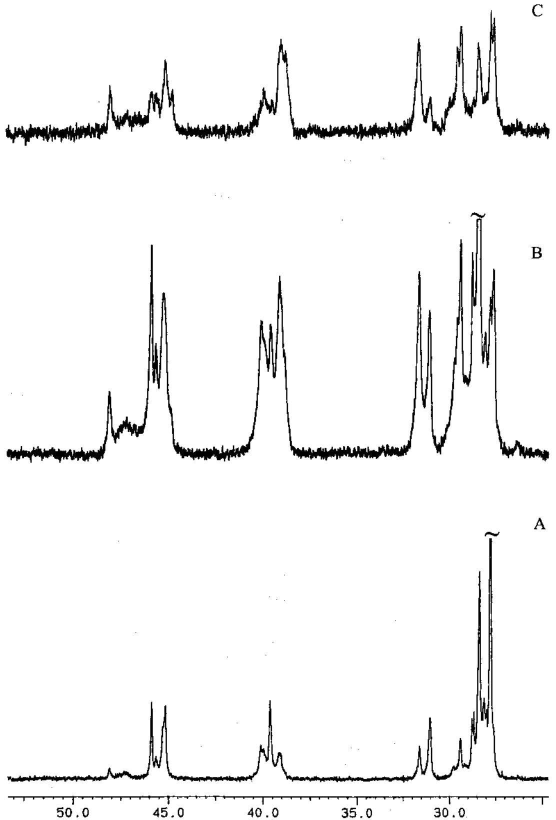


Figure 7. ^{13}C NMR spectra of E−N copolymers prepared with $Me_2C(Flu)CpZrCl_2$ (**4**), with N mole percent: 25% (A); 58% (B); 62% (C).

$$f(\mathrm{E}) = f_\mathrm{E}(\mathrm{alt}) + f_\mathrm{E}(\mathrm{isl}) = f(m) + f(r) + f_\mathrm{E}(\mathrm{isl}) \quad (7)$$

$$f_\mathrm{E}(\mathrm{isl}) = \sum_{i=0}(2+i)f_i = 2f_0 + 3f_1 + 4f_2 + ... = (2+x)f(\mathrm{isl}) \quad (8)$$

where f_i is the molar fraction of sequences formed by an N followed by $2 + i$ E's, and $2 + x$ is the average length of the isolated sequences, with $x \geq 0$.

The total N content is given by

$$f(\mathrm{N}) = f_\mathrm{N}(\mathrm{block}) + f_\mathrm{N}(\mathrm{diad}) + f_\mathrm{N}(\mathrm{alt}) + f_\mathrm{N}(\mathrm{isl}) \quad (9)$$

$$f_\mathrm{N}(\mathrm{diad}) = 2f(\mathrm{diad}) \quad (10)$$

$$f_\mathrm{N}(\mathrm{block}) = \{\sum_{i=1}(2+i)[\mathrm{E{-}N{-}N_{\mathit{i}}{-}N{-}E}]\}/\{[\mathrm{N}] + [\mathrm{E}]\} = (3+y)f(\mathrm{block}) \quad (11)$$

where $3 + y$ is the average length of blocks (including triads), with $y \geq 0$.

One can see that

$$f_\mathrm{N}(\mathrm{alt}) = f_\mathrm{N}(m) + f_\mathrm{N}(r) = \{\,[\mathrm{N{-}E{-}N{-}E{-}N}] + {}^1/_2[\mathrm{E{-}E{-}N{-}E{-}N}]\}/\{[\mathrm{N}] + [\mathrm{E}]\} \quad (12)$$

$$f_\mathrm{N}(\mathrm{isl}) = \{[\mathrm{E{-}E{-}N{-}E{-}E}] + {}^1/_2[\mathrm{E{-}E{-}N{-}E\text{-}N}]\}/\{[\mathrm{N}] + [\mathrm{E}]\} \quad (13)$$

while

$$f_\mathrm{E}(\mathrm{alt}) = \{[\mathrm{N{-}E{-}N{-}E{-}N}] + {}^1/_2[\mathrm{E{-}E{-}N{-}E{-}N}] + {}^1/_2[\mathrm{N{-}N{-}E{-}N}]\,\}/\{[\mathrm{N}] + [\mathrm{E}]\} = f_\mathrm{N}(\mathrm{alt}) + {}^1/_2[\mathrm{N{-}N{-}E{-}N}]/\{[\mathrm{N}] + [\mathrm{E}]\} \quad (14)$$

$$f(\mathrm{isl}) = \{[\mathrm{E{-}E{-}N{-}E{-}E}] + {}^1/_2[\mathrm{E{-}E{-}N{-}E{-}N}] + {}^1/_2[\mathrm{N{-}N{-}E{-}E}]\,\}/\{[\mathrm{N}] + [\mathrm{E}]\} = f_\mathrm{N}(\mathrm{isl}) + {}^1/_2[\mathrm{N{-}N{-}E{-}E}]/\{[\mathrm{N}] + [\mathrm{E}]\} \quad (15)$$

and that

$$f(\mathrm{diad}) + f(\mathrm{block}) = \{{}^1/_2[\mathrm{N{-}N{-}E{-}N}] + {}^1/_2[\mathrm{N{-}N{-}E{-}E}]\}/\{[\mathrm{N}] + [\mathrm{E}]\} \quad (16)$$

By combining this equation with eqs 12−15, we obtain the relationship

$$f(\mathrm{diad}) + f(\mathrm{block}) = f(m) + f(r) + f(\mathrm{isl}) - (f_\mathrm{N}(m) + f_\mathrm{N}(r) + f_\mathrm{N}(\mathrm{isl})) = \Delta f(m) + \Delta f(r) + \Delta f(\mathrm{isl}) \quad (17)$$

Finally, our previous assignments allow us to distinguish among E−E... sequences of different lengths, having defined f_i in eqs 3 and 9 as the molar fractions of N units followed by $2 + i$ E units.

When only short EE sequences are present (see Figure 9A−C), we observe that

$$\text{for the N−E-E−N sequence: } f_0 = f(\mathrm{S}_{\alpha\delta}) = f(\mathrm{S}_{\beta\gamma}) \quad (18)$$

$$\text{for the N−E−E−E−N sequence: } f_1 = f(\mathrm{S}_{\alpha\zeta}) = f(\mathrm{S}_{\beta\epsilon}) = f(\mathrm{S}_{\gamma\delta}) \quad (19)$$

$$\text{for the N−E−E−E−E−N sequence: } f_2 = f(\mathrm{S}_{\delta\epsilon}) \quad (20)$$

Although in a few examples of mainly alternating copolymers we could describe the E sequences considering only the three terms f_0, f_1, and f_2 (whence f(isl) and f_E(isl) could be computed), in general we consider the variables f(isl), f_E(isl), and f_0 (from eq 18), while the signals considered in eqs 19 and 20 contain contributions arising from longer E sequences (see Figure 9D), so that these equations are replaced by

$$f(\mathrm{S}_{\alpha\delta+}) = f(\mathrm{S}_{\beta\delta+}) = f(\mathrm{S}_{\gamma\gamma+}) = f(\mathrm{isl}) - f_0 \quad (19')$$

$$f(\mathrm{S}_{\delta\delta+}) = f(\mathrm{isl}) - f_0 - f_1 \quad (20')$$

$$f(\mathrm{S}_{\delta+\delta+}) = f_\mathrm{E}(\mathrm{isl}) - 4f(\mathrm{isl}) + 2f_0 + f_1 \quad (21)$$

When the two peaks $f(\mathrm{S}_{\delta\delta+})$ and $f(\mathrm{S}_{\delta+\delta+})$ are measured distinctly, then the variable f_1 contained in eq 20′ must be considered; otherwise, the sum of eqs 20′ and 21 provides

$$f(\mathrm{S}_{\delta\delta+}) + f(\mathrm{S}_{\delta+\delta+}) = f_\mathrm{E}(\mathrm{isl}) - 3f(\mathrm{isl}) + f_0 \quad (22)$$

and f_1 is not needed.

Choice of Variables. We choose the variables, depending on the characteristics of a given copolymer, among the following quantities defined above: $f(m)$, $f(r)$, f(isl), f_E(isl), f_0, $f(M)$, $f(R)$, f(block), f_N(block), $\Delta f(m)$, $\Delta f(r)$, Δf(isl). We discussed above the possible use of f_1 and f_2.

Constraints. The number of independent variables *nv* is then reduced by a certain number of constraints. Equations 2 and 17 represent two constraints to be

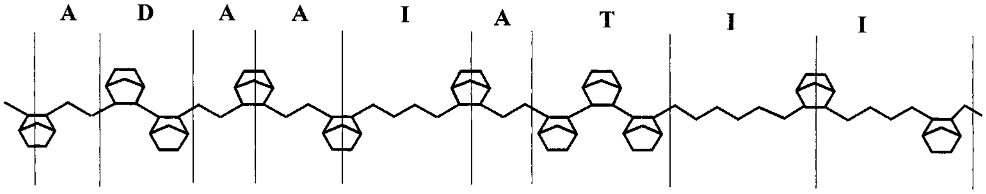


Figure 8. A random E−N copolymer chain.

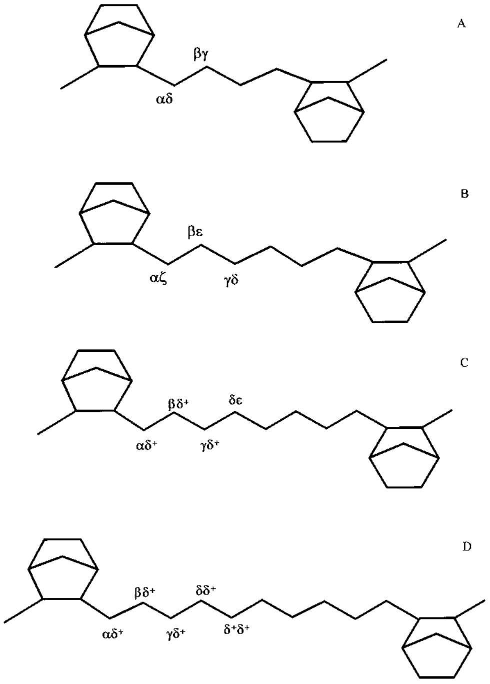


Figure 9. Carbon nomenclature in ethylene blocks: N−E−E−N (A), N−E−E−E-N (B), N−E−E−E−E−N (C), N−E−E−E−E−N (D).

satisfied always. Moreover, in copolymers containing a small amount of blocks we can assume that these are formed purely by triads; hence

$$f_{\mathrm{N}}(\text{block}) = 3f(\text{block}) \tag{23}$$

Finally, to reduce *nv* we assume that

$$\Delta f(m){:}\Delta f(r){:}\Delta f(\text{isl}) = f(m){:}f(r){:}f(\text{isl}) \tag{24}$$

which is equivalent to stating that diads and blocks have the same probability of following (and preceding) an alternating or an isolated sequence. Hence, only $\Delta f(m)$ is considered and *nv* is reduced by 1 or 2. We should also add that a solution must meet further conditions in order to be accepted, namely

$$f_0 < f(\text{isl}) \text{ (from eq 4)}$$

$$x, y \geq 0 \text{ (eqs 8 and 11)}$$

$$\Delta f(m), \Delta f(r), \Delta f(\text{isl}) \geq 0 \text{ (eq 17)}$$

Results and Discussion

Analysis of ^{13}C NMR Spectra. The procedure described in the previous section was used to analyze the ^{13}C NMR spectra of a great number of E−N copolymers having N content ranging from 1 to 56 mol %, prepared with catalysts **1−4.** Examples of the complete spectra are displayed in Figures 4−7. We note that chemical shifts of a given signal in copolymers prepared with the same catalyst were found to be identical or to differ by less than ±0.05 ppm. The application of the procedure provided the molar fractions of the various stereosequences for each sample as well as an advancement in the chemical shift assignments. The final assignments are listed in Table 2.

Here, we present a few examples of the analysis of ^{13}C NMR spectra of copolymers prepared with various catalysts: *KM103* (catalyst **2**), *KM108* (**3**), and *KM55* and *KM65* (**1**). The spectra of copolymer samples prepared with **2** (*KM103*) and **3** (*KM108*) are displayed in Figures 10 and 11, respectively. The spectra of the two copolymers obtained from **1** (*KM55* and *KM65*) are shown in Figures 12 and 13. Their norbornene content ranges from 43 to 52 mol %. The spectra with a lower norbornene content are simpler, while those with very high norbornene content are too complex and are beyond the scope of this work.

In Table 2 all the data for each of the four spectra are reported. Column 1 lists all the values observed for the chemical shifts, while column 2 gives the corresponding assignments for each type of signals as either derived from previous works or achieved in the present work (in bold). Column 1 of each section (A, B, C, D) lists the chemical shifts of the signals observed in the given spectrum. The normalized peak areas of distinguishable signals observed in each spectrum are given in the second column of each section.

Tables 3−6 present the observed and calculated values of the normalized peak areas for each distinct and measurable group of signals, along with the carbon types from which the signals arise. For each datum we also report the coefficients of the independent and dependent variables considered. The best fitting for the molar fractions and their standard deviations are given at the bottom of the table, together with the average length of isolated sequences. In the four examples considered here we assume that blocks longer than triads are absent.

a. Microstructure of the Copolymers Prepared with *rac*-Me$_2$Si(2-Me-benz[*e*]indenyl)$_2$ZrCl$_2$ (*KM103*). The complete ^{13}C NMR spectrum of an E−N copolymer prepared with *rac*-Me$_2$Si(2-Me-benz[*e*]indenyl)$_2$ZrCl$_2$ (**2**) activated with methylaluminoxane (MAO) is reported in Figure 10, while the chemical shifts of all the observed signals, along with the normalized peak areas of groups of signals which will be used for the calculation, are listed in Table 2, column A. The norbornene content of this copolymer is 43.64 mol %, estimated as the ratio between the average intensities for carbons C1, C2, and C7 and the total intensity for the CH$_2$ carbons (carbons C5 and E):

$$f(\mathrm{N}) = \frac{[\mathrm{N}]}{[\mathrm{N}]+[\mathrm{E}]} = \frac{\frac{1}{3}(I_{\mathrm{C1}} + I_{\mathrm{C2}} + 2I_{\mathrm{C7}})}{I_{\mathrm{CH_2}}}$$

Considering that norbornene content is ca. 44 mol % and the integrals of the resonances of norbornene in

Table 2. Chemical Shifts (ppm) and Peak Areas of the Assigned Signals for the Spectra of Four E−N Copolymer Samples

		A (*KM 103*) $f(\mathrm{N}) = 0.436$		B (*KM 108*) $f(\mathrm{N}) = 0.435$		C (*KM 55*) $f(\mathrm{N}) = 0.479$		D (*KM 65*) $f(\mathrm{N}) = 0.522$	
CH_2 chemical shifts	assignt	chemical shifts	$I/I_{\mathrm{tot\ CH_2}}$[a]	chemical shifts	$I/I_{\mathrm{tot\ CH_2}}$[a]	chemical shifts	$I/I_{\mathrm{tot\ CH_2}}$[a]	chemical shifts	$I/I_{\mathrm{tot\ CH_2}}$[a]
26.24	C5 D *M*	26.23	0.0055	26.22	0.0044	26.22	0.0941	26.22	0.1227
26.59	C5 T	26.54/59	0.0207						
27.20	C5 T							27.22	0.0091
27.39/43	C5 D *R*							27.41	0.0108
27.58	C5 D *R*							27.50	0.0052
27.73	$S_{\delta+\delta+}$ or T *MR*	27.72	0.0680	27.72	0.0142	27.72	0.0311	27.72	0.0231
27.80	$S_{\delta\delta+}$			27.82	0.0067	27.83	∧		
27.95	$S_{\beta\delta+}$	27.97	∨			27.97	0.0188		
28.04	$S_{\alpha\beta}$ *r*			28.04	0.1870				
28.07	$S\gamma\gamma^+$					28.08	∨	28.07	0.0446
28.13	$S_{\alpha\delta+}$	28.13	∨			28.14	0.0561		
28.20	$S_{\alpha\delta}$								
28.30	C5/C6	28.32	0.5371	28.32	0.5943	28.32	0.3137	28.32	0.3004
28.41	$S_{\beta\gamma}$	28.43	∧			28.44	0.0494	28.45	∨
28.52	$S_{\alpha\beta}$ *m*[b]					28.52	0.0288	28.52	0.0528
28.59	$S_{\alpha\beta}$ *m*[b]								
28.63	$S_{\alpha\beta}$ *m*[b]	28.63	∨	28.63	∨				
28.68	$S_{\alpha\beta}$ *m*[b]					28.67	∨	28.67	∨
28.73	$S_{\alpha\beta}$ *m*[b]	28.72	0.2798	28.72	0.1781	28.73	0.1435	28.73	0.1270
28.82	$S_{\alpha\beta}$ *m*[b]								
28.87	$S_{\alpha\beta}$ *m*[b]					28.87	0.0760	28.87	∨
29.00	$S_{\alpha\beta}$ *m*[b]					29.00	0.0548	29.00	0.1454
29.11	$S_{\alpha\beta}$ *m*[b]	29.09	0.0156						
29.37	C6 D *R*			29.37	0.0047				
29.37	C6 T					29.30	0.0309	29.30	0.0348
29.49	C6 T	29.50	0.0493	29.50	0.0021				
29.56									
29.68	C6 D *M*			29.69	0.0085	29.67	0.1028	29.67	0.1242
29.77									
29.88	C6 T	29.88	0.0240						
29.95	T								
30.16									
C7 chemical shifts	assignt	chemical shifts	$I/I_{\mathrm{tot\ C7}} \times f(\mathrm{N})$[a]	chemical shifts	$I/I_{\mathrm{tot\ C7}} \times f(\mathrm{N})$[a]	chemical shifts	$I/I_{\mathrm{tot\ C7}} \times f(\mathrm{N})$[a]	chemical shifts	$I/I_{\mathrm{totC7}} \times f(\mathrm{N})$[a]
30.50	T								
30.58	T	30.57	0.0253						
30.77									
30.90	I								
30.98	A *m*	30.98	∨	30.98	0.4144	30.98	0.1195	30.98	∨
31.05	A *m*	31.05	0.3715	31.27	0.0098	31.05	0.1512	31.05	0.3263
31.17	D *M*			31.38	0.0035	31.16	0.0476		
31.32	D *M*			31.57	0.0072	31.31	0.1566	31.31	0.1960
31.57	D *R*								
33.07	T	33.06	0.0396			33.07	0.0039		
C1−C4 chemical shifts	assignt	chemical shifts	$I/I_{\mathrm{tot\ C1-C4}} \times f(\mathrm{N})$[a]	chemical shifts	$I/I_{\mathrm{tot\ C1-C4}} \times f(\mathrm{N})$[a]	chemical shifts	$I/I_{\mathrm{tot\ C1-C4}} \times f(\mathrm{N})$[a]	chemical shifts	$I/I_{\mathrm{tot\ C1-C4}} \times f(\mathrm{N})$
34.34	T					34.34	0.0033	34.33	0.0073
34.92	T	34.86/91	0.0203						
35.18	T					35.18	0.0032	35.18	0.0071
35.70	T					35.72	0.0054	35.73	0.0068
36.74	T	36.78	∨			36.88			
36.94	T	36.94	0.0209						
37.87	T					37.87		37.87	0.0097
38.93	D *R*/T	38.94	0.0091						
39.05	T			39.08	0.0069				
39.27/38	T	39.37	∨	39.32	0.0091				
39.50	I			39.50	∨				
39.54	A *r*			39.53	0.2362				
39.62		39.59	0.1008			39.59	0.0731	39.56	0.0655
39.88	D *M*	39.88	0.0730	39.87	∨	39.85	∨	39.85	∨
39.90	A *m*			40.01	0.1827	39.90	0.2163	39.90	0.2355
40.04	A *m*	40.02	0.1691			40.03	0.1066	40.03	0.0944
40.43	D *M*					40.43	0.0709	40.41	0.0893
40.62		40.61	∨			40.66			
40.80	T	40.78	0.0210						
41.01						41.07		41.06	0.0064
41.13						41.16			
41.23									
41.32	T	41.32	∨						
41.45	T	41.43	0.0217			41.43			
41.56	T	41.57	∧						

Table 2 (Continued)

C2−C3 chemical shifts	assignt	chemical shifts	$I/I_{\text{tot C2−C3}} \times f(\text{N})^a$	chemical shifts	$I/I_{\text{tot C2−C3}} \times f(\text{N})^a$	chemical shifts	$I/I_{\text{tot C2−C3}} \times f(\text{N})$	chemical shifts	$I/I_{\text{tot C2−C3}} \times f(\text{N})^a$
42.56									
42.97		42.97	0.0063						
43.24									
43.72									
44.01		44.04	0.0063						
44.17									
44.80								44.80	0.0022
45.07	I			45.05	∨				
45.14	I	45.11	0.0901	45.14	∨	45.14	0.0586	45.13	0.0379
45.21	A *r*			45.21	0.2493				
45.32						45.37	0.0042		
45.42/53	T	45.40	0.0137	45.54	0.0120			45.42	0.0106
45.62	D *R*								
45.73	A *m*					45.73	0.0714	45.72	0.0829
45.82	A *m*	45.80	0.2531	45.79	0.1641	45.79	0.1572	45.80	0.1405
45.96	D *M*					45.96	0.0227		
46.05	D *M*			46.01	0.0054	46.02	0.0631	46.02	0.0981
46.23								46.23	0.0073
46.33									
46.50	D *M*	46.50	∨	46.55	0.0024	46.50	0.0228	46.50	0.0223
46.63	D *M*	46.64	0.0160						
46.70	D *M*	46.78	∧						
46.91									
47.11	D *M*	47.10	0.0133	47.12	0.0019	47.08	0.0736	47.09	0.1066
47.27/32	D *M*					47.34	0.0051		
47.66									
48.07	D *R*								
48.2									
48.52									
48.99									
49.34	T								
49.56	T	49.53						49.36	0.0067
49.80	T	49.79	0.0198						
50.00	T								
52.70	T	52.68	∨						
52.80		52.81	0.0175						
53.05		53.05	∧						
53.44	T							53.44	0.0073

[a] *I* is the measured peak area. Symbols ∨ and ∧ indicate that the area was included in the normalized peak area below or above, respectively. A few very small peaks, where the normalized area is not given, were not included in the calculation. [b] The chemical shift of *meso* $S_{\alpha\beta}$ is sensitive to adjacent units sequences; see the discussion in the text.

diads and in blocks are rather small, this copolymer is mainly alternating. Of all the variables, eight are necessary for the description of this spectrum; we chose $f(m)$, $f(M)$, f_0, $f(\text{isl})$, and $f_E(\text{isl})$ as independent variables, while the other three ($\Delta f(m)$, $f(\text{block})$, and $\Delta f(\text{isl})$) are dependent due to the relationships 2, 17, 23, and 24 described above. In this case relationship 23 was assumed due to the very low content of norbornene blocks.

The first row of Table 3 reports the total norbornene molar fraction described in terms of the selected variables by combining eqs 9, 10, 11, and 17, i.e.

$$f_N = f(m) - \Delta f(m) + f(\text{isl}) - \Delta f(\text{isl}) + 2f(M) + 3f(\text{block})$$

hence, the coefficients for this equation are 1, −1, 1, −1, 2, and 3 for $f(m)$, $\Delta f(m)$, $f(\text{isl})$, $\Delta f(\text{isl})$, $f(M)$, and $f(\text{block})$, respectively.

As in Table 2, we start from the right side of the spectrum. The resonance at 26.23 ppm is due to carbon C5 (*external*) of the *meso* ENNE sequence, while the *internal* C6 resonates at 29.88 ppm and is included in the group of signals between 29.37 and 29.88 ppm. The normalized peak area observed is 0.009; the coefficient 2 for the independent variable $f(M)$ derives from

$$f_N(\text{diad}) = 2f(\text{diad}) \tag{10}$$

In this spectrum the resonances of signals $S_{\delta\delta+}$ and $S_{\delta+\delta+}$ are not distinct, so the second row gives the sum of $f(\delta\delta^+)$ and $f(\delta^+\delta^+)$ which is derived from

$$f(S_{\delta\delta+}) + f(S_{\delta+\delta+}) = f_E(\text{isl}) - 3f(\text{isl}) + f_0 \tag{22}$$

The coefficients for this equation are 1, −3, and 1 for $f_E(\text{isl})$, $f(\text{isl})$, and f_0, respectively.

The signals from 27.97 to 28.43 ppm, corresponding to $S_{\beta\delta+}$, $S_{\gamma\gamma+}$, $S_{\alpha\delta+}$, $S_{\alpha\delta}$, $S_{\beta\gamma}$, and C5/C6(isl) and C5/C6(alt), are not distinct enough, and they have been integrated together. Since from eqs 18, 19, and 19′ we obtain

$$f(S_{\beta\delta+}) + f(S_{\gamma\gamma+}) + f(S_{\alpha\delta+}) + f(S_{\alpha\delta}) + f(S_{\beta\gamma}) = 2f(S_{\alpha\delta}) + 3f(S_{\alpha\delta+}) = 3f(\text{isl}) - f_0$$

and

$$f_N(m) = f(m) - \Delta f(m) \quad \text{and} \quad f_N(\text{isl}) = f(\text{isl}) - \Delta f(\text{isl})$$

the normalized peak area, found to be 0.53, corresponds to

$$f_N(m) + f_N(\text{isl}) + 2f(S_{\alpha\delta}) + 3f(S_{\alpha\delta+}) = f(m) - \Delta f(m) + f_N(\text{isl}) + 4f(\text{isl}) - \Delta f(\text{isl}) - f_0$$

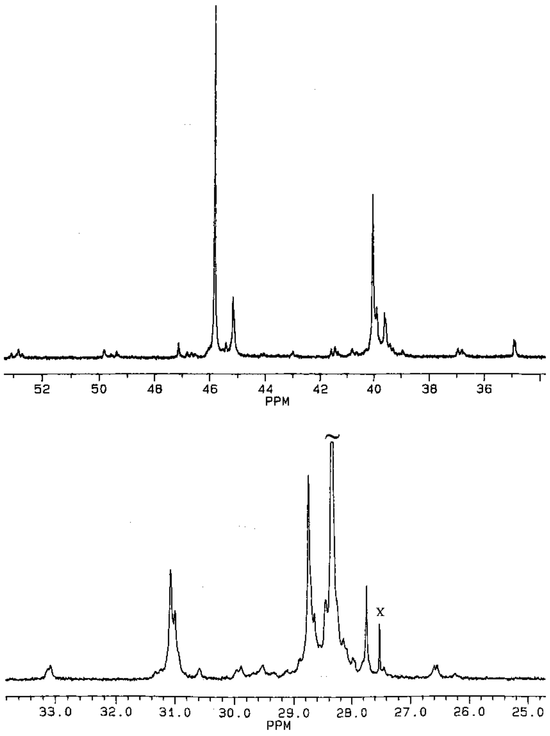


Figure 10. ^{13}C NMR spectrum of a copolymer sample *KM103* prepared with *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]indenyl)_2ZrCl_2$ (**2**).

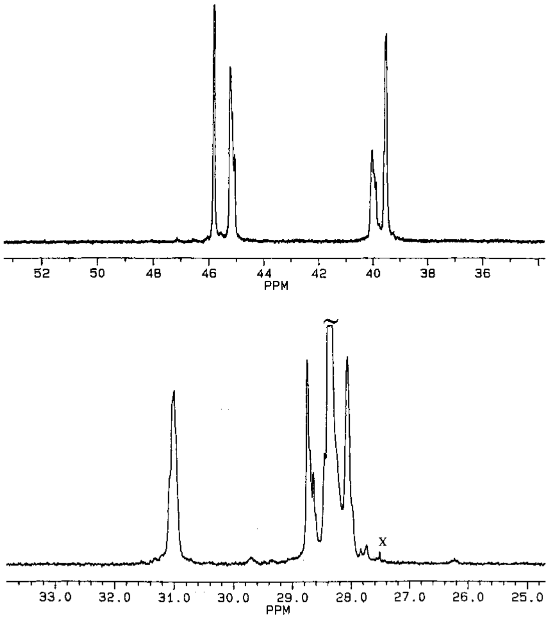


Figure 11. ^{13}C NMR spectrum of a copolymer sample *KM108* prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**3**).

Thus, the coefficients for this equation are 1, −1, 1, 4, −1, and −1 for $f(m)$, $\Delta f(m)$, $f_N(\text{isl})$, $f(\text{isl})$, $\Delta f(\text{isl})$, and f_0, respectively.

The fraction $f(m)$ is obtained from the peak areas of the signals between 28.52 and 29.00 ppm. In the subsequent row $f(\text{block})$ represents the sum of (i) the integrals of the signal at 26.59 ppm assigned to the external C5 of a *MM* triad; (ii) all the integrals of the resonances from 29.37 to 29.88 ppm (which we assume to be due to triads), less the area of the signal at 26.23 ppm of the external C5 of *meso* diads, since these resonances include also the signal at 29.68 ppm due to the internal C6 of *meso* diads, as already mentioned; and (iii) the area of the signals at 27.43−27.50 ppm which we assign to the external signal of the *racemic* side of a *MR* triad. (From the integral of these signals we subtract the integral of a signal at 21.37 ppm which, along with the peak marked with X on the spectrum in Figure 10, is due to unidentified products of decomposition reactions occurring at the high temperature of the NMR experiment in $C_2D_2Cl_4$ solvent.[20]) The coefficient for the dependent variable $f(\text{block})$ is 3 since we assume that this copolymer does not contain norbornene blocks longer than triads.

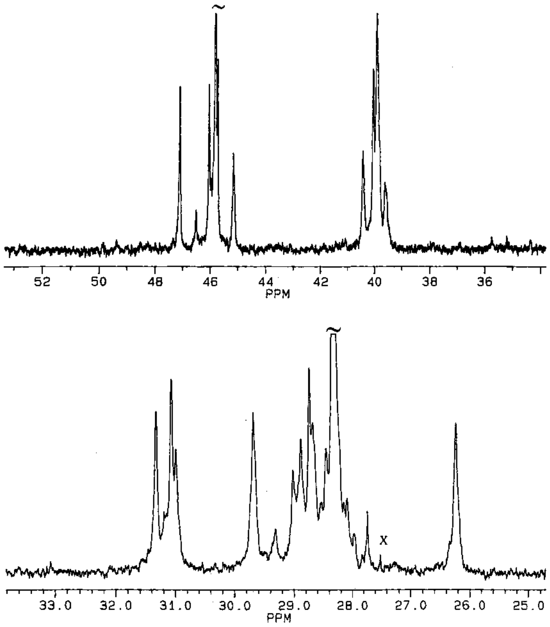


Figure 12. ^{13}C NMR spectrum of copolymer sample *KM55* obtained from *rac*-$Et(indenyl)_2ZrCl_2$ (**1**).

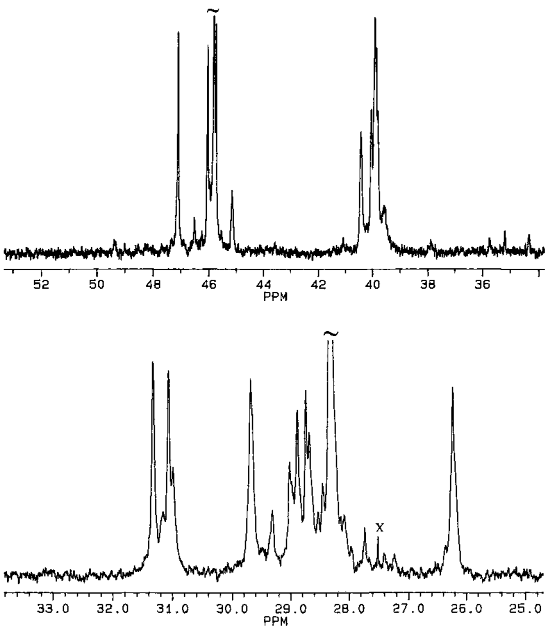


Figure 13. ^{13}C NMR spectrum of copolymer sample *KM65* obtained from *rac*-$Et(indenyl)_2ZrCl_2$ (**1**).

Similar equations can be written for the molar fractions corresponding to the other signals. Stoichiometric considerations lead us to conclude that the signal at 33.06 ppm arises from the carbon C7 of triads. The integrals of C7 signals have not been used since the overlapping of the resonances of C7 carbons of various

Table 3. Least-Squares Fitting of ^{13}C NMR Signals for Sample *KM103* Produced with Catalyst *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]indenyl)_2ZrCl_2$ (2)

		normalized peak area		independent variables					dependent variables		
	carbon	obsd	calcd	$f(m)$	f_0	$f(\text{isl})$	$f_E(\text{isl})$	$f(M)$	$\Delta f(m)$	$f(\text{block})$	$\Delta f(\text{isl})$
$f(N)$		0.436	0.441	1.0	0.0	1.0	0.0	2.0	−1.0	3.0	−1.0
$f_N(M)$	CH_2	0.011	0.008	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
$f(\delta\delta^+) + f(\delta^+\delta^+)$	CH_2	0.068	0.077	0.0	1.0	−3.0	1.0	0.0	0.0	0.0	0.0
$f_N(m) + f_N(\text{isl}) + 2f(\alpha\delta) + 3f(\alpha\delta^+)$	CH_2	0.537	0.546	1.0	−1.0	4.0	0.0	0.0	−1.0	0.0	−1.0
$f(m)$	CH_2	0.295	0.278	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$f_N(\text{block})$	CH_2	0.094	0.091	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
$f_N(m) + f_N(M)$	C1	0.242	0.260	1.0	0.0	0.0	0.0	2.0	−1.0	0.0	0.0
$f_N(\text{block})$	C1	0.093	0.091	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
$f_N(\text{isl})$	C1	0.101	0.090	0.0	0.0	1.0	0.0	0.0	0.0	0.0	−1.0
$f_N(\text{isl})$	C2	0.090	0.090	0.0	0.0	1.0	0.0	0.0	0.0	0.0	−1.0
$f_N(m)$	C2	0.253	0.252	1.0	0.0	0.0	0.0	0.0	−1.0	0.0	0.0
$f_N(M)$	C2	0.013	0.008	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
$f_N(\text{block})$	C2	0.080	0.091	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
av length of isolated				0.277[a]	0.095	0.099	0.281	0.004	0.025	0.030	0.009
sequences = 2.82.				0.006[b]	0.026	0.007	0.010	0.004			
$R^2 = 0.9997$											

[a] Best-fitting molar fractions. [b] Deviations.

Table 4. Least-Squares Fitting of ^{13}C NMR Signals for *KM108* Produced with catalyst *rac*-$Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (3)

		normalized peak area		independent variables							dependent variables			
	carbon	obsd	calcd	$f(m)$	$f(r)$	f_0	$f(\text{isl})$	$f_E(\text{isl})$	$f(M)$	$f(R)$	$\Delta f(m)$	$\Delta f(r)$	$f(\text{block})$	$\Delta f(\text{isl})$
$f(N)$		0.435	0.436	1.0	1.0	0.0	1.0	0.0	2.0	2.0	0.0	0.0	3.0	−1.0
$f_N(M)$	CH_2	0.009	0.009	0.0	0.0	0.0	0.0	0.0	2.0	−1.0	−1.0	0.0	0.0	0.0
$f(\delta\delta^+) + f(\delta^+\delta^+)$	CH_2	0.021	0.022	0.0	0.0	1.0	−3.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
$f(\alpha\delta^+) + f(\beta\delta^+) + f(\gamma\gamma^+) + f(r)$	CH_2	0.186	0.187	0.0	1.0	−3.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$f_N(m) + f_N(r) + f_N(\text{isl}) + 2f(\alpha\delta)$	CH_2	0.591	0.592	1.0	1.0	2.0	1.0	0.0	0.0	0.0	−1.0	−1.0	0.0	−1.0
$f(m)$	CH_2	0.177	0.174	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$f_N(R)$	CH_2	0.009	0.009	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
$f_N(\text{block})$	CH_2	0.006	0.005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
$f_N(m) + f_N(M)$	C1	0.182	0.180	1.0	0.0	0.0	0.0	0.0	2.0	0.0	−1.0	0.0	0.0	0.0
$f_N(\text{isl}) + f_N(r)$	C1	0.236	0.242	0.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	−1.0	0.0	−1.0
$f_N(\text{block}) + f_N(R)$	C1	0.016	0.015	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	3.0	0.0
$f_N(\text{block}) + f_N(R)$	C2	0.012	0.015	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	3.0	0.0
$f_N(\text{isl}) + f_N(\text{r})$	C2	0.249	0.242	0.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	−1.0	0.0	−1.0
$f_N(m) + f(M)$	C2	0.169	0.174	1.0	0.0	0.0	0.0	0.0	1.0	0.0	−1.0	0.0	0.0	0.0
$f(M)$	C2	0.004	0.005	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
av length of isolated				0.175[a]	0.144	0.090	0.105	0.245	0.005	0.004	0.005	0.004	0.002	0.003
sequences = 2.34				0.003[b]	0.005	0.002	0.004	0.008	0.002	0.002				
$R^2 = 0.9999$														

[a] Best fitting molar fractions. [b] Deviations.

sequences decrease the accuracy of the least-squares fitting. The signals at 34.86/34.91, 36.78/36.98, 38.94, 40.61/40.78, and 41.57 ppm have been tentatively assigned to Cl/C4 carbons of triads; hence, the sum of all their integrals yields 3f(block). Although in this spectrum the peak of alternating *meso* sequences is distinguished, we sum up the contributions corresponding to the two independent variables $f_N(m)$ and $f_N(M)$ in one equation, owing to a partial overlapping of the areas. In the C2/C3 region the distinct resonances of the signals 45.11 and 45.82 ppm allow us to estimate accurate values of f(isl) and $f_N(m)$, respectively; $f_N(M)$ has been estimated from the peak areas of signals at 47.1 ppm, and f(block) has been estimated from the sum of signals at 42.97, 44.04, 45.4, 49.79, and 53.5 ppm.

Table 3 shows that the deviation of the calculated normalized peak areas of each equation is not greater than 2.5%. Our assumptions are supported by the low estimated standard deviation of each molar fraction, on the order of 1% except for the deviation of 2.5% for variable f_0.

b. Microstructure of the Copolymers Prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (*KM108*). This copolymer contains 43.5 mol % of norbornene and almost no diads or longer NNN sequences; thus, it is mainly alternating, as is apparent in Figure 11 from the absence of all the small signals due to norbornene diads or triads present in Figure 10 and in Table 2, column A. Nevertheless, the NMR spectrum is quite different from the spectrum of the mainly alternating copolymer prepared with *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]indenyl)_2ZrCl_2$ discussed above, owing to the presence of NEN *racemic* sequences and to the absence of triads. Eleven variables are necessary to describe this spectrum: in addition to the five independent variables $f(m)$, $f(M)$, f_0, f(isl), and f_E(isl) chosen for *KM103*, here also $f(r)$ and $f(R)$ are needed as independent variables. Thus, $f(r)$ was estimated from the CH_2, C1, and C2 signals; e.g., considering the CH_2 region, we have introduced $f(r)$ in the fourth equation. Moreover, in this case the distinction of more details leads to a larger number of equations. This results in much lower deviations of the calculated

Table 5. Least-Squares Fitting of ^{13}C NMR Signals for Sample *KM55* Produced with Catalyst *rac*-Et(indenyl)$_2$ZrCl$_2$ (1)

		normalized peak area		independent variables					dependent variables		
	carbon	obsd	calcd	$f(m)$	f_0	f(isl)	f_E(isl)	$f(M)$	$\Delta f(m)$	f(block)	Δf(isl)
f(N)		0.479	0.484	1.0	0.0	1.0	0.0	2.0	−1.0	3.0	−1.0
$f_N(M)$	CH$_2$	0.188	0.184	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
$f(\delta\delta^+) + f(\delta^+\delta^+)$	CH$_2$	0.031	0.034	0.0	1.0	−3.0	1.0	0.0	0.0	0.0	0.0
$f(\beta\delta^+)$	CH$_2$	0.019	0.030	0.0	−1.0	1.0	0.0	0.0	0.0	0.0	0.0
$f(\alpha\delta^+) + f(\gamma\gamma+)$	CH$_2$	0.056	0.060	0.0	−2.0	2.0	0.0	0.0	0.0	0.0	0.0
$f_N(m) + f_N(\mathrm{isl}) + f(\alpha\delta) + f(\beta\gamma)$	CH$_2$	0.363	0.372	1.0	2.0	1.0	0.0	0.0	−1.0	0.0	−1.0
$f(m)$	CH$_2$	0.274	0.287	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
f_N(block)	CH$_2$	0.040	0.034	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
f_N(isl)	C1	0.073	0.060	0.0	0.0	1.0	0.0	0.0	0.0	0.0	−1.0
$f_N(m) + f_N(M)$	C1	0.394	0.390	1.0	0.0	0.0	0.0	2.0	−1.0	0.0	0.0
f_N(block)	C1	0.012	0.033	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
f_N (isl)	C2	0.073	0.060	0.0	0.0	1.0	0.0	0.0	0.0	0.0	−1.0
$f_N(m)$	C2	0.228	0.207	1.0	0.0	0.0	0.0	0.0	−1.0	0.0	0.0
f_N (M)	C2	0.187	0.183	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
f_N(block)	C2	0.059	0.033	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
av length of isolated sequences = 2.77					0.287[a]	0.052	0.083	0.230	0.092	0.080	0.011
					0.008[b]	0.006	0.005	0.012	0.005		
$R^2 = 0.9994$											

[a] Best fitting molar fractions. [b] Deviations.

Table 6. Least-Squares Fitting of ^{13}C NMR Signals for Sample *KM65* Produced with Catalyst *rac*-Et(indenyl)$_2$ZrCl$_2$ (1)

		normalized peak area		independent variables					dependent variables		
	carbon	obs	calcd	$f(m)$	f(isl)	f_E(isl)	$f(M)$	$f(R)$	$\Delta f(m)$	f(block)	Δf(isl)
f(N)		0.522	0.536	1.0	1.0	0.0	2.0	2.0	−1.0	3.0	−1.0
$f_N(M)$	CH$_2$	0.247	0.217	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
f_N (R)	CH$_2$	0.022	0.021	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
$f_E(\mathrm{isl}) + f_N(m) + f_N(\mathrm{isl})$	CH$_2$	0.370	0.391	1.0	1.0	1.0	0.0	0.0	−1.0	0.0	−1.0
$f(m)$	CH$_2$	0.327	0.336	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
f_N(block)	CH$_2$	0.035	0.035	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
f_N (isl)	C1	0.066	0.039	0.0	1.0	0.0	0.0	0.0	0.0	0.0	−1.0
f_N (m)	C1	0.241	0.225	1.0	0.0	0.0	0.0	0.0	−1.0	0.0	0.0
$f_N(M)$	C1	0.179	0.217	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
f_N(block)	C1	0.037	0.035	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
f_N (isl)	C2	0.038	0.038	0.0	1.0	0.0	0.0	0.0	0.0	0.0	−1.0
f_N (m)	C2	0.223	0.222	1.0	0.0	0.0	0.0	0.0	−1.0	0.0	0.0
$f_N(M)$	C2	0.227	0.217	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
f_N(block)	C2	0.034	0.035	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
av length of isolated sequences = 2.23				0.336[a]	0.057	0.128	0.109	0.011	0.111	0.011	0.019
				0.010[b]	0.012	0.018	0.006	0.008			
$R^2 = 0.9998$											

[a] Best fitting molar fractions. [b] Deviations.

normalized peak areas and in an accurate definition of the molar fractions.

c. Microstructure of the Copolymers Prepared with *rac*-Et(indenyl)$_2$ZrCl$_2$ *(KM55 and KM65).* The spectra of copolymers reported in Figures 12 and 13 have been analyzed with the above methodology. Both copolymers *KM55* and *KM65* contain a quite high norbornene content (47.9 and 52.2 mol %, respectively). Both contain NN diads and triads. *KM55* is described with the same variables as *KM103,* but here the better resolution of the CH$_2$ region of the spectrum allows to write a greater number of equations. The calculated molar fractions show a very low standard deviation.

On the contrary, in the case of sample *KM65,* owing to the higher norbornene content and the higher level of diads, the inclusion of $f(R)$ among the variables is needed to improve the fitting of the intensities. The area of the signal at 27.43 ppm is used to estimate $f(R)$. However, in this case it was not possible to determine f_0, and all contributions from isolated ethylene carbons are summed up in the fourth equation of Table 6.

Comparison of Controversial Assignments of Signals of Alternating N−E−N and of N−E−E−N Carbons. The results of a statistical treatment of stereoregular and stereoirregular alternating ethylenenorbornene copolymers allowed us to evidence major conformational differences depending on the *meso*/*racemic* configuration of the N−E−N sequence.[15] The conformational interpretation of the ^{13}C NMR chemical shifts led to the following predictions: (a) the two methines C2, C1 of the cyclic unit and the ethylene CH$_2$ show two distinct ^{13}C NMR signals in regularly alternating *isotactic* and *syndiotactic* copolymers, the latter being shifted upfield for all the three carbons; (b) the isolated signals of the two methines of an N unit in a N−E−E... sequence and the $S_{\alpha\delta}$ signal are shifted upfield with respect to the signals of isotactic alternating signals and occur close to the syndiotactic alternating ones; (c) the $S_{\beta\gamma}$ and $S_{\gamma\delta}$ signals are shifted low field with respect to $S_{\beta\epsilon}$ e and $S_{\delta\epsilon}$, respectively.

A close inspection of the chemical shifts and peak areas of spectra prepared in the presence of catalyst precursors **1, 2,** and **3** confirmed the above predictions and led to the assignments reported in Table 1 and in ref 15.

While these studies were completed, the results of the efforts of other groups in assigning ^{13}C NMR spectra of E−N copolymers have appeared in the literature.[17−19]

Table 7. Comparison between Recent Assignments of the Ethylene CH_2 Signals

	carbon	chemical[a] shifts (ppm) ref 15	Δδ	carbon	chemical[b] shifts (ppm) ref 18	Δδ	carbon	chemical[b] shifts (ppm) ref 19	Δδ
1	$S_{\delta+\delta+}$	27.73	0	$S_{\delta+\delta+}$	29.92	0	$S_{\delta+\delta+}$	29.9	0
2	$S_{\delta\delta+}$	27.80	0.07	$S_{\delta\delta+}$	30.00	0.08			
3	$S_{\beta\delta+}$	27.95	0.22	$S_{\beta\delta+}$	30.12	0.20	$S_{\delta\delta+}$, $S_{\gamma\delta+}$	30.1	0.2
	$S_{\alpha\beta}$ *r*	28.04	0.31						
4	$S_{\gamma\delta}$, $S_{\gamma\delta+}$	28.07	0.34	$S_{\gamma\delta+}$	30.24	0.32	$S_{\beta\delta+}$, $S_{\gamma\delta}$	30.3	0.4
5	$S_{\alpha\delta+}$	28.13	0.40	$S_{\alpha\delta+}$	30.31	0.39			
6	$S_{\alpha\delta}$	28.20	0.47	$S_{\gamma\delta}$	30.38	0.46			
7	C5/C6	28.32	0.59	C5/C6	30.44	0.52	C5/C6, $S_{\alpha\beta}$	30.5	0.6
8	$S_{\beta\gamma}$	28.41	0.68	$S_{\beta\gamma}$	30.54	0.62			
9	$S_{\alpha\beta}$ *m*	28.63	0.90	$S_{\alpha\delta}$	30.77	0.85	$S_{\alpha\delta+}$	30.8	0.9
10	$S_{\alpha\beta}$ *m*	28.74	1.01	$S_{\alpha\beta}$ *m*	30.90	0.98	$S_{\alpha\delta+\beta}$	30.9	1.0

[a] Chemical shifts referred to HMDS. [b] Chemical shifts referred to TMS.

In Table 7 our assignments and the observed chemical shifts in the ethylene CH_2 region are compared with those by Fink and co-workers[18] and by Arndt-Rosenau and Beulich.[19] Fink has distinguished and assigned the resonances of ethylene carbons by comparing the ^{13}C NMR spectra of copolymers containing ^{13}C-enriched ethylene or ^{13}C-enriched norbornene with those of copolymers prepared with monomers having natural ^{13}C abundance. Arndt's assignments are based on the comparison of spectra of copolymers of naturally ^{13}C-enriched monomers with various compositions obtained with different catalysts, in a manner analogous to our previous analysis.

As clear from Table 7, Fink observes the same number of signals as we do, apart from the $S_{\alpha\beta}$ *racemic* signal. There is agreement on the assignments of signals 1 ($S_{\delta+\delta+}$), 2 ($S_{\delta\delta+}$), 3 ($S_{\beta\delta+}$), 5, ($S_{\alpha\delta+}$), 7 (C5/C6), 8 ($S_{\beta\gamma}$), and 10 ($S_{\alpha\beta}$). Three differences concern the assignment of signals 4, 6, and 9: (1) We include $S_{\gamma\delta}$ and $S_{\gamma\delta+}$ in signal 4 at 28.07 ppm, while Fink assigns $S_{\gamma\delta}$ to signal 6 shifted 0.14 ppm low field with respect to signal 4 that we both assign to $S_{\gamma\delta+}$. (2) In our assignment $S_{\alpha\delta}$ (signal 6) is shifted 0.07 ppm low field with respect to $S_{\alpha\delta+}$ (signal 5 for us and for Fink), while according to Fink $S_{\alpha\delta}$ is shifted 0.39 ppm low field with respect to signal 5. (3) We assign signal 9 ($S_{\alpha\delta}$ according to Fink) to a fine splitting of $S_{\alpha\beta}$.

As mentioned earlier, our assignments were obtained by combining indications derived from calculations of the conformer populations with experimental observations. The calculations were not able to predict the small differences (ca. 0.07 ppm) between the resonances of $S_{\delta\delta+}$ and $S_{\delta+\delta+}$ and between those of $S_{\alpha\delta}$ and $S_{\alpha\delta+}$, which arise from a slight increase in the gauche conformer populations as the distance of the observed E carbon from N increases or when the number of ethylene units separating two N's increases from two to three. Thus, a similar small difference (on the order of 0.07 ppm) cannot be ruled out between the signals of $S_{\gamma\delta}$ and $S_{\gamma\delta+}$ (while we assign signal 4 to both these carbons). However, the large low-field shift (0.39 ppm) of $S_{\alpha\delta}$ with respect to $S_{\alpha\delta+}$, as proposed by Fink, is not justified by the calculations. On the other hand, our assignment of signal 9 to alternating ethylene carbons adjacent to isolated units (sequences NEN*E*NEE and EEN*E*NEE) is fully justified by the increase of the intensity of peak 10 relative to 9 in samples with increasing N content, this corresponding to an increase of the regularly alternating NEN*E*NEN sequences. Since the three differences in the assignments are interconnected, we are confident in the correctness of our previous interpretation.[15]

Arndt-Rosenau and Beulich[19] observe only a limited number (five) of ethylene signals. This is partly due to the low resolution of their spectra but is also consistent with the absence of such sequences as NEEN predicted by the polymerization mechanism proposed by them. Indeed, the lack of signals at $\Delta\delta = 0.5$ and $\Delta\delta = 0.7$ ppm in Table 7 agrees with our assignment of such resonances to $S_{\alpha\delta}$ and $S_{\alpha\delta+}$, in contrast with Fink's assignment.

To further clarify the controversial region of the ethylene CH_2 signals, the procedure for the analysis of the spectra described above has been used by assuming the three different assignments for a few E−N copolymer spectra. It was found that Arndt's description of the CH_2 region, as reported in Table 2 of ref 19, is too poor to be applied to high-resolution spectra, since it allows for several arbitrary choices. Thus, the comparison was restricted to Fink's and our assignments. In all the cases examined, a better least-squares fitting of the experimental peak areas resulted with our interpretation. Table 8 shows as examples the results obtained with samples *LB92* and *KM53*. For the sake of brevity, only the data corresponding to different assignments are presented together with the overall rms deviation and R^2. The lower part of the table shows that the two choices lead to differences in the molar fractions on the order of 2%, while the standard deviations of the solutions are nearly one-half with the present assignments.

We already reported on the assignments of signals of C2/C3 and C5/C6 norbornene carbons of isotactic and syndiotactic E−N−N−E sequences.[13−15] More recently, Arndt[19] reported quite similar assignments; hence, no disagreement exists among the authors on the interpretation of these signals.

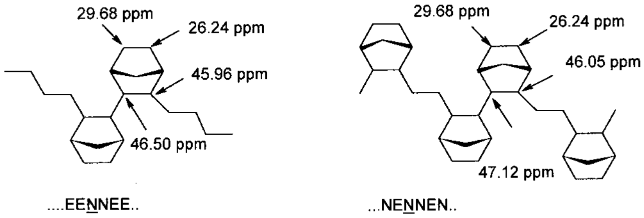
New Assignments of ^{13}C NMR Signals of Ethylene−Norbornene Copolymers. The analysis of the spectra discussed above is based on hypotheses concerning novel assignments of signals and on verifying the consistency of the hypotheses with the experimental intensities of the signals and the stoichiometric requirements of the copolymer chain. The generally low deviations found between the calculated intensities and the observed values first of all has confirmed our previous assignments of (i) the signals of ethylene-centered sequences; (ii) the *meso* and *racemic* signals of alternating NEN; and (iii) the C5/C6, C2/C3, C1/C4, and C7 signals of isotactic and syndiotactic ENNE blocks. Moreover, the analysis has allowed us to extend the assignments.

The main achievement is represented by the assignments of novel signals of the ENNE diad in the C2/C3

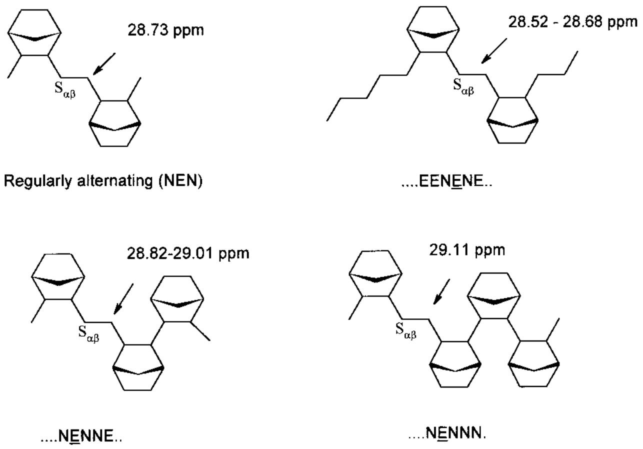
Table 8. Comparison between Least-Squares Fittings of Normalized Peak Areas Assuming Different Signal Assignments

LB 92						KM 53					
	ref 15			ref 18			ref 15			ref 18	
assignt	obs	calcd	assignt	obs	calcd	assignt	obs	calcd	assignt	obs	calcd
$f(m)$	0.124	0.129	$f(m)$	0.065	0.114	$f_N(\mathrm{alt}) + f_N(\mathrm{isl}) + f(\mathrm{S}\alpha\delta)$	0.367	0.367	$f_N(\mathrm{alt}) + f_N(\mathrm{isl})$	0.367	0.310
$f(\mathrm{S}\alpha\delta)$	0.091	0.101	$f(\mathrm{S}\alpha\delta)$	0.059	0.086	$f(m)$	0.263	0.245	$f(m) + f(\mathrm{S}\alpha\delta)$	0.263	0.311
$f(\mathrm{S}\gamma\delta)+ f(\mathrm{S}\gamma\delta+)$	0.066	0.080	$f(\mathrm{S}\gamma\delta)$	0.091	0.062						
			$f(\mathrm{S}\gamma\delta+)$	0.066	0.037						
rsmd (%)	0.67			2.07			0.91			2.31	
R^2 (%)	99.99			99.91			99.98			99.87	
Molar Fractions (%)						Molar Fractions (%)					
$f(m)$	12.9 ± 0.4			11.4 ± 1.2		$f(m)$	24.5 ± 0.6			24.1 ± 1.5	
f_0	10.1 ± 0.4			8.6 ± 1.3		f_0	7.2 ± 0.5			7.0 ± 1.6	
f_1	-			6.2 ± 1.8		$f(\mathrm{isl})$	11.6 ± 0.4			12.2 ± 1.2	
$f(\mathrm{isl})$	18.1 ± 0.3			18.6 ± 0.9		$f_E(\mathrm{isl})$	32.9 ± 0.9			34.3 ± 2.4	
$f_E(\mathrm{isl})$	54.9 ± 0.6			57.3 ± 1.8		$f(R)$	1.0 ± 0.4			0.2 ± 1.1	

Scheme 1



Scheme 2



region. The complexity of these signals shows that they are pentad or even hexad sensitive.

(1) A new pair of signals at 45.96 and 46.50 ppm is evidenced in the spectra of E−N copolymers prepared with *rac*-Et(indenyl)$_2$ZrCl$_2$ catalyst precursor having norbornene content between 30 and 45 mol %. The sum of the peak areas of these signals and of those already reported at 46.05 and 47.12 ppm corresponds to $f_N(\mathrm{diad}) = 2f(\mathrm{diad})$ and to twice the integral of the C5 signal of the isotactic ENNE diad at 26.24 ppm. It is worth pointing out that this signal, being in a quite open window of the spectrum, is one of those yielding the most accurate information on the molar fractions of copolymer sequences. Since, as we evidenced earlier,[15] the strong difference between the internal C6 and external C5 carbons of *meso* ENNE diads is originated by the distortions of the two adjacent rings, it is reasonable that these carbons do not feel effects of units located beyond the next ethylene, while the diad carbons C2/C3 may be affected by conformational differences. Such a behavior is depicted in Scheme 1.

(2) A second important result is the first assignment of a few signals due to carbons in ENNNE triads:

(i) The signal at 26.59 ppm is assigned to the external C5 carbons of a *MM* or *MR* triad. This assignment was suggested by the proximity of this signal to 26.24 ppm, the resonance of the external C5 carbons of *meso* ENNE diads. This seems to indicate that ring distortions in triads have a small further effect on the external C5 relative to the diads C5. Also, this signal, being well distinguishable as the above-mentioned *meso* diad signal at 26.24 ppm, allows us to estimate the quantity $2f(MM) + f(MR)$.

(ii) The signal at 27.73 ppm is due to the external C5 carbons of the *racemic* side of the *MR* triad, being very close to 27.52 ppm, the resonance of the external C5 of racemic ENNE diads. When no *racemic* ENNE diads are present, i.e., when their characteristic C2/C3 signals at 48.05 and 45.62 ppm are absent, the sum of the integrals of the signals at 27.73 and 26.59 ppm yields $f(\mathrm{block})$. The molar fraction of blocks is quite an important parameter, since it allows us to obtain the average length of norbomene blocks in a given copolymer.

(iii) The internal signals of *MM* and *MR* triads or of longer blocks from our calculations appear in the region between 29.3 and 29.9 ppm, that is, overlap the internal C6 of *meso* and *racemic* ENNE sequences.

(iv) The signal at 33.07 ppm and the signal at 34.34 ppm have been assigned to C7 and to Cl/C4 of triads, respectively.

(3) As already mentioned in the previous section, carbons $\mathrm{S}_{\alpha\beta}$ of an alternating *meso* EN*E*NE sequence are sensitive to the type of sequences close to the next ethylene unit. Scheme 2 evidences the variation of chemical shifts of the signals in this region of the spectra associated with the presence of adjacent EE, EEE, NN, and NNN sequences in polymers with different norbornene contents. This interpretation was deduced by inspection of the range 28.5−29.1 ppm of the spectra of various samples and was confirmed by the corresponding molar fraction calculations.

Conclusions

We have presented a best-fitting procedure for computing the molar fractions of the stereosequences which define the microstructure of an ethylene−norbornene copolymer, utilizing the observed intensities of the assigned signals of ^{13}C NMR spectra and accounting for the stoichiometric requirements of the chain. Application of the procedure to a large number of E−N copolymers prepared with four different catalysts allowed us (a) to estimate the molar fractions of the various components with a standard deviation on the order of 1–2%, (b) to compare the signal assignments reported in the literature and to confirm our previous assignments, and (c) to assign new signals, such as those of the C2/C3 carbons of a EENNEE *meso* sequence and of the external carbons C5 of *MM* and *MR* triads in ENNNE sequences.

The extension of this method to samples with a very high norbornene content should lead to further assignments of NMR chemical shifts in longer norbornene blocks and to a thorough investigation of the E–N chain. On the other hand, the quantitative determination of the microstructure of these copolymers will allow us to progress in clarifying the polymerization mechanism. An application of the method to the study of the thermochemical characteristics of the E–N copolymers will be presented elsewhere.

Experimental Section

General Conditions. All experiments and manipulations involving air-sensitive compounds were carried out under a dry nitrogen atmosphere in a glovebox or using standard Schlenk line techniques. MAO (30 wt % as toluene solution, Witco) was used after removing all volatiles and drying the resulting powder by warming (50 °C) for 3 h in vacuo (0.1 mmHg). Toluene was dried and distilled from sodium under a nitrogen atmosphere. *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**) was purchased from Witco while Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**3**) and Me$_2$C(Flu)(Cp)ZrCl$_2$ (**4**) were kindly provided by MONTELL. Norbornene was dried and distilled over sodium. Ethylene was passed over molecular sieves and BTS salts (Fluka) to remove oxygen and water.

Ethylene–Norbornene Copolymerizations. In a typical experiment, a 250 mL round-bottomed Schlenk flask containing toluene as a solvent was charged with a known amount of MAO as toluene solution and norbornene (total volume = 100 mL). After evacuation, the solution was saturated with ethylene at atmospheric pressure at 30 °C. Then the zirconocene as toluene solution was introduced in order to reach the zirconocene concentration of 8×10^{-5} mol/L and [MAO]/[Zr] molar ratio of 1000. The copolymerization reaction was stopped before 10% of the starting norbornene was consumed by adding acidified methanol. Polymers were precipitated by pouring the reactor contents into acidic EtOH and stirring overnight. Finally, the polymer was filtered, washed with EtOH, and dried at 50–60 °C in a vacuum oven.

^{13}C NMR Analysis. Copolymer samples were dissolved in C$_2$D$_2$Cl$_4$ solvent using HMDS as internal reference. The NMR spectra were obtained using a Bruker AM-270 spectrometer operating at 67.89 MHz (^{13}C) direct observation, in the PFT mode at 103 °C. Gated decoupling experiments with preirradiation of the protons before the ^{13}C pulse have been performed to ensure equal NOE's throughout the NMR spectra.[22,23] A 90° pulse of 10.5 μs was employed with a repetition of 21 s. A window of 10 870 Hz was observed, typically accumulating from 800 to 8000 free induction decays on 64K of computer memory. CPD (composite pulse decoupling) was used to remove ^{13}C–^{1}H couplings. The copolymer norbornene content was calculated from the integrals (*I*) of ethylene and norbornene carbons as follows:

$$f(\mathrm{N}) = \frac{[\mathrm{N}]}{[\mathrm{N}] + [\mathrm{E}]} = \frac{\frac{1}{3}(I_{\mathrm{C1}} + I_{\mathrm{C2}} + 2I_{\mathrm{C7}})}{I_{\mathrm{CH_2}}}$$

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Supporting Information Available: Table reporting all the chemical shifts of spectra of a wide selection of copolymers prepared with catalysts **1**–**4** and containing an increasing amount of norbornene, including the peak area of each distinguishable signal or group of signals observed in each spectrum and final assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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