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Alternating Isotactic Ethylene−Norbornene Copolymers by C_1-Symmetric Metallocenes: Determination of the Copolymerization Parameters and Mechanistic Considerations on the Basis of Pentad Analysis

Incoronata Tritto,* Laura Boggioni,† and Dino R. Ferro‡

Istituto per lo Studio delle Macromolecole, Consiglio Nazionale delle Ricerche, Via E. Bassini 15, I-20133 Milano, Italy

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ABSTRACT: The copolymerization of ethylene and norbornene by catalytic systems composed of *i*-Pr-[(3-R−Cp)(Flu)]$ZrCl_2$ (R = Me or Pr^i) and methylaluminoxane was investigated. Isotactic, alternating ethylene−norbornene (E−N) copolymers with percentages of pentads NENEN up to 21% and norbornene incorporation up to 40% were obtained. NEENE sequences were observed in copolymers synthesized with both metallocenes. The microstructural analysis by ^{13}C NMR of such alternating isotactic copolymers was completely obtained at pentad level by a methodology that exploits all the peak areas of the spectra and accounts for the stoichoimetric requirements of the copolymer chain. Such a methodology has allowed us to reconsider some controversial assignments of ethylene CH_2 signals. The present understanding of E−N copolymer NMR spectra at the pentad level has allowed us to test the statistical model best describing E−N copolymerization with C_1 symmetric catalysts and to study the influence of ligand substitution of these catalysts on the polymerization mechanism. The root-mean-square deviations between experimental and calculated pentads demonstrate that the two-site alternating mechanism is not valid. Penultimate (second-order Markov) effects play a decisive role in E−N copolymerizations with *i*-Pr[(3-Pr^i−Cp)(Flu)]-$ZrCl_2$ (**2**). The first-order Markov model is sufficient to describe the microstructure of E−N copolymers with *i*-Pr[(3-Me−Cp)(Flu)]$ZrCl_2$ (**3**) at least at not too high N/E feed ratios. It is concluded that in E−N copolymerizations with these catalysts, both N and E are inserted at the same open site. Norbornene undergoes a Cossee's migratory insertion and after every insertion the copolymer chain backskips to its original position. The synthesis of alternating E−N copolymers, possible only at very high N/E feed ratios, derives from the impossibility of having two consecutive norbornene insertions. The isotacticity is a consequence of norbornene insertion always at the same site with the same face. The steric interactions between the growing polymer chain and the methyl Cp substituent of **3** and the isopropyl Cp substituent of **2** appear to be important to determine the copolymerization statistics.

Introduction

The development of well-defined metallocene catalysts has created great opportunities for controlling poly-α-olefin stereospecificity and properties.[1] Intense efforts have been undertaken to elucidate the mechanisms operating in these catalytic systems. The analysis of the stereochemistry of α-olefin polymerization has proven to provide new insights into the mechanistic details of catalytic olefin polymerization. The synthesis of syndiotactic polypropylene with C_s-symmetric $R_2C[(Cp)(9\text{-}Flu)]ZrCl_2$[2] and of hemiisotactic polypropylene with C_1-symmetric $R_2C[(3\text{-}RCp)(9\text{-}Flu)]ZrCl_2$[3] is one of the evidences for Cossee's[4] *alternating mechanism* (Figure 1).[5] The mechanism involves a migration of the polymer chain during insertion from one site to another. Thus, the position formerly occupied by the polymer chain is available for the next incoming olefin. According to the alternative proposed *retention mechanism*, the olefin approaches the metallocene always from the same site either because of a nonmigratory insertion or because the chain migrates as in Cossee's mechanism and then skips back to its original position.

Copolymerization of two or more different monomers presents further opportunities for tailoring polymer structures and properties. The catalyst can select different monomer units in defined sequences and insert them stereoselectively into the polymer chain.

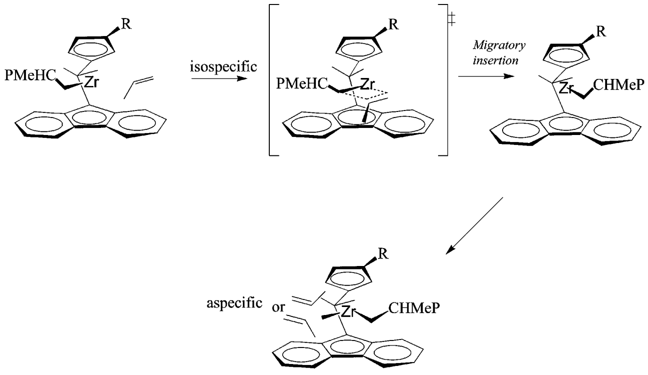

Figure 1. Two-site alternating "switching" insertion mechanism (TSAM)[7,8]

Several groups have exploited the dual coordination sites of C_1-symmetric metallocenes to obtain interesting new stereoregular ethylene−α-olefin copolymers. The preparation of highly alternating isotactic ethylene−α-olefin copolymers from bridged C_1-symmetric metallocenes with two heterotopic sites such as $R_2C[(3\text{-}RCp)(9\text{-}Flu)]ZrCl_2$[7,8] has been interpreted as one of the most convincing evidences that support the alternating mechanism. This mechanism involves the alternating

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

† E-mail: boggioni@ismac.cnr.it.

‡ E-mail: ferro@ismac.cnr.it.

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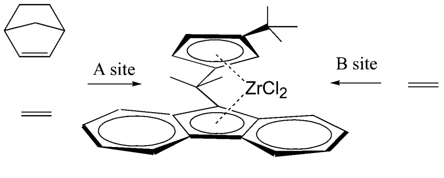
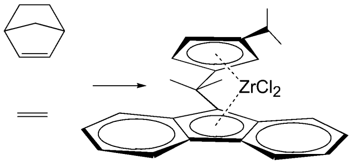


Two-Sites Alternating Mechanism (TSAM)



Retention mechanism

Figure 2. Proposed mechanisms for alternating isotactic E−N copolymerization with C_1-metallocenes: two-site alternating mechanism (TSAM);[9] retention mechanism.[12]

insertion of olefins at the two heterotopic sites which selectively insert one or both olefins. An alternating "switching-site" kinetic model employing different kinetic selectivity at the two heterotopic sites of these metallocenes was developed and found to simulate well the copolymer sequence distribution.

Arndt,[9] Fink,[10] and Harrington[11] sought to exploit the dual coordination sites of C_1-symmetric metallocenes to control the sequence specificity in ethylene (E)−norbornene (N) copolymerization. E−N copolymers are a new interesting class of polymers with special thermoplastic properties, high transparency, and high glass transition temperature, imparted by the norbornene component. Highly alternating isotactic E−N copolymers have been obtained. The microstructure of these copolymers has been analyzed and used to evaluate olefin polymerization mechanisms. With respect to propene homo- and copolymerization, the analysis of the microstructures of E−N copolymers has the advantage that regioerrors are not possible and stereoerrors cannot result from isomerization processes of the growing polymer chain. Arndt et al.[9] investigated the mechanism of the alternating ethylene−norbornene copolymers obtained by i-Pr(3-Bu^t−Cp)(Flu)ZrCl$_2$ (**1**) and methylaluminoxane (MAO). By applying the retention and alternating mechanisms to the observed copolymer microstructures, they concluded that E−N copolymerization at 30 °C proceeds by an *alternating mechanism* (Figure 2). More recently, Fink and co-workers[12,13] found that the microstructure of the copolymers produced with catalyst i-Pr(3-Pr^i−Cp)(Flu)ZrCl$_2$ (**2**) and MAO is consistent with a *retention mechanism.*

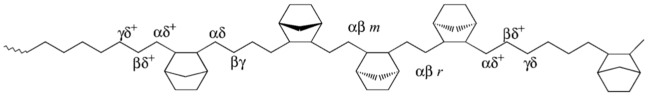


Figure 3. Copolymer chain and nomenclature.

The full exploitation of the information contained in the copolymer ^{13}C NMR spectra and the correct assignment of these spectra are crucial for utilizing copolymer microstructure to gain deeper insight into the polymerization mechanism. Our group[14−20] has devoted considerable effort to the synthesis and the study of the microstructure of E−N copolymers by ^{13}C NMR. A typical E−N copolymer chain, containing norbornene in alternating sequences (differences in stereochemistry are also considered) or norbornene isolated between ethylene blocks, is sketched in Figure 3, along with the adopted carbon numbering and denomination. There is now quite a general agreement on assignments of ^{13}C NMR spectra of alternating copolymers. The progress in such assignments has been reviewed by Fink.[12] However, there is still disagreement on the assignments of a couple of signals in the CH$_2$ region. Assignments are summarized in Table 1, already published in ref 17, and shown in Figure 4.

This paper will present our most recent studies regarding the microstructural analysis by ^{13}C NMR of alternating isotactic copolymers obtained with metallocenes **2** and i-Pr(3-Me−Cp)(Flu)ZrCl$_2$ (**3**). Our results on copolymer microstructures obtained at *pentad* level will be discussed and used to evaluate and test the copolymerization statistical models. Both our and Fink's assignments for the carbons of the CH$_2$ region (Table 1) were used to determine the pentad information and to test the polymerization mechanism: the results will be compared and discussed.

Detailed information on the polymerization mechanisms operating in these systems has been obtained, since it has been possible to clearly discriminate between alternating and retention mechanisms.

Results

Copolymer Synthesis. Two metallocenes (Figure 5) were investigated to obtain evidence in favor of one of the proposed olefin polymerization mechanisms: alternating and retention.

Ethylene−norbornene copolymerizations were conducted at 30 °C at atmospheric ethylene pressure in the presence of methylaluminoxane at [Al]/[Zr] molar ratio

Table 1. Comparison between Recent Assignments of the Ethylene CH$_2$ Signals

	carbon	chemical[a] shifts (ppm)[17]	Δδ	carbon	chemical[b] shifts (ppm)[13]	Δδ	carbon	chemical[b] shifts (ppm)[9]	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.

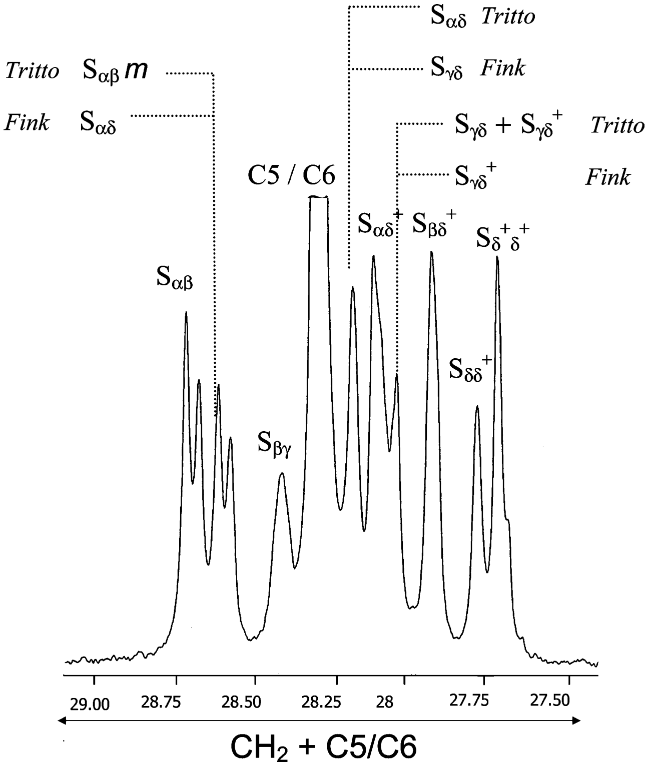
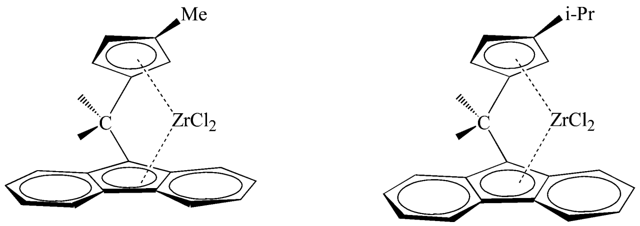


Figure 4. Differences in assignments of alternating isotactic E−N copolymers.



3 2

Figure 5. Metallocenes under investigation *i*-Pr(3-Me−Cp)(Flu)ZrCl$_2$, (**3**) *i*-Pr(3-Pr^i−Cp)(Flu)ZrCl$_2$ (**2**).

of 3000. A wide range of [N]/[E] feed ratios was employed. The polymerization tests were not designed to investigate the activity of the catalytic systems, but rather to have low comonomer conversion and low polymer concentration in the polymerization medium, that is, to ensure the conditions required for the study of copolymer microstructures. Norbornene conversion was kept below 10%. The norbornene content in the copolymer was obtained by ^{13}C NMR spectroscopy. Molecular weights were estimated by GPC measurements. The results concerning the synthesis and the characterization of selected copolymers are summarized in Table 2. Polymer yields of copolymerization with **2** are of the same order of magnitude of those reported by Fink.[12] Productivities with these two catalysts increase along with the increase of hindrance of the R substituent (Me < *i*-Pr) under the experimental conditions used. Similarly, Waymouth[7] observed a slight increase in activity in E−P copolymerization from the unsubstituted metallocene (R = H) to the methyl-substituted one, **3**. The nature of the cyclopentadienyl substituent also has an influence on the behavior of copolymerization: at a similar feed ratio (compare entries 5−8 and 14−17 and see plot in Figure 6) the isopropyl-substituted metallocene incorporates less norbornene than the methyl-substituted catalyst.

Table 2. Ethylene−Norbornene Copolymerizations with the Catalysts *i*-Pr(3-Pr^i−Cp)(Flu)ZrCl$_2$ (2) and *i*-Pr(3-Me−Cp)(Flu)ZrCl$_2$ (3): Mole Percent of Norbornene in the Copolymer, Productivity, and Molecular Weight[a]

entry	metallocene	feed ratio [N]/[E]	*N*, mol %[b]	activity[c]	M_n[d] × 10^3	M_w/M_n
1	**3**	0.12		539	37.60	2.9
2	**3**	0.23		231	49.56	2.4
3	**3**	0.39		397	54.01	2.5
4	**3**	0.63	15.98	570	56.81	2.6
5	**3**	0.92	20.41	458		
6	**3**	1.36	26.59	745	83.93	2.3
7	**3**	3.62	35.64	948	96.27	2.6
8	**3**	8.29		101	71.05	2.6
9	**3**	17.66	40.50	39	76.72	2.4
10	**2**	0.06		2186	21.56	2.3
11	**2**	0.16		2484	19.83	3.0
12	**2**	0.28	8.82	1587	28.18	2.4
13	**2**	0.43	11.35	2781	37.52	2.7
14	**2**	0.96	21.54	3455		
15	**2**	2.33	24.04	4163	89.29	2.6
16	**2**	4.00	31.20	3670	102.29	2.7
17	**2**	9.00	39.80	8679	90.96	2.7

[a] Toluene as a solvent, MAO as a cocatalyst, 30 °C, P_E = 1.01 atm. [b] Mole percent of norbornene calculated by analysis of ^{13}C NMR spectra (see text). [c] Activity = kg of polymer/(mol of Zr h). [d] Measured by GPC at 145 °C in 1,2-dichlorobenzene.

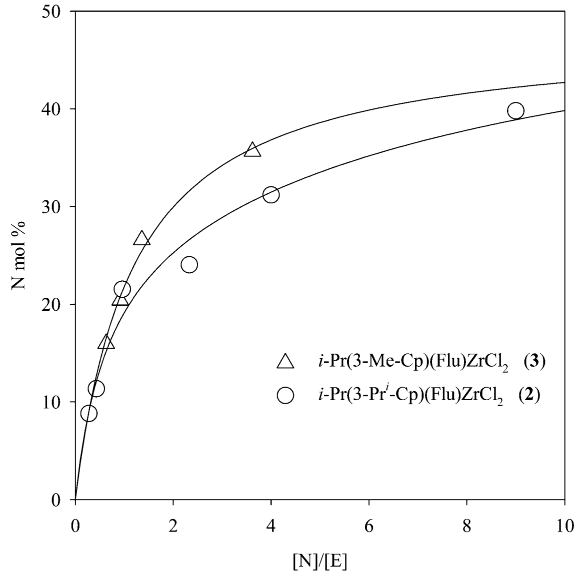


Figure 6. Plot of norbornene content vs N/E feed ratio of E−N copolymers of Table 2.

Differences in the polymerization time used, which varies from one copolymerization to the other in order to keep low comonomer conversion, may have an influence on molecular weight. This could mask the effect of Cp substituents on the molecular weight of copolymers of the two series. Thus, it is not possible to draw any conclusion on the effect of the Cp substituent on chain transfers.

^{13}C NMR Analysis. The spectra of two samples of E−N copolymers, with similar norbornene content, prepared with metallocenes **2** and **3** are compared in Figures 7A and 7B, respectively. Entry no. 17 has 39.8 mol % of norbornene, while entry no. 9 has 40.5 mol %. The **2** and **3** precatalysts, in combination with MAO under the polymerization conditions used, produce only isolated and alternating sequences. Thus, the spectra

Table 3. Assignments of ^{13}C Chemical Shifts for Carbons of Norbornene and Ethylene Units in E−N Copolymers

	carbon	chemical shift^a(ppm)	sequences
		Ethylene^b	
$S_{\delta+\delta+}$	CH_2	27.74	EEE*E*EEE
$S_{\delta\delta+}$	CH_2	27.80	ENE*E*EE
$S_{\beta\delta+}$	CH_2	27.93	EN*E*EE
$S_{\gamma\gamma+}{}^c$	CH_2	28.05	ENE*E*E
$S_{\alpha\delta+}$	CH_2	28.13	EN*E*EE
$S_{\alpha\delta}$	CH_2	28.18	EN*E*EN
$S_{\beta\gamma}$	CH_2	28.39	EN*E*EN
$S_{\alpha\beta}$	CH_2	28.56	EEN*E*NEE
$S_{\alpha\beta}$	CH_2	28.61	NEN*E*NEE
$S_{\alpha\beta}$	CH_2	28.66	NEN*E*NEE
$S_{\alpha\beta}$	CH_2	28.70	NEN*E*NEN
		Norbornene	
	C5/C6	28.33	E*N*E
	C7	30.89	EE*N*EE
	C7	30.96	NE*N*EE
	C7	31.04	NE*N*EN
	C1/C4	39.54	½NE*N*EE
	C1/C4	39.57	EE*N*EE
	C1/C4	39.86	½NE*N*EE
	C1/C4	40.00	NE*N*EN
	C2/C3	45.09	½NE*N*EE
	C2/C3	45.13	EE*N*EE
	C2/C3	45.78	½NE*N*EE + NE*N*EN

[a] The ^{13}C NMR spectra were measured in $C_2D_2Cl_4$ at 105 °C, chemical shifts are referred to HMDS. [b] The Greek subscripts indicate the distance of the observed secondary carbon atom S from the closest norbornene carbons. [c] In the assignment by Tritto et al.,[17] symbol $S_{\gamma\gamma+}$ includes signal $S_{\gamma\delta}$ as well as the signals indicated by $S_{\gamma\delta+}$.

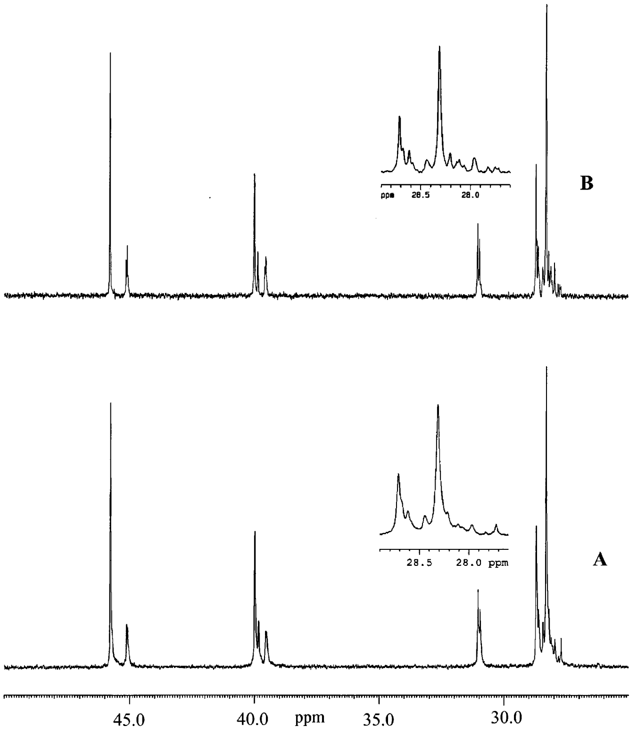


Figure 7. Spectra of two samples of E−N copolymers, with similar norbornene content, prepared with metallocenes **2** (A), entry no. 17 with N content of 39.8 mol %, and **3** (B), entry no. 9 with N content of 40.5 mol %.

are relatively simple due to the prevailingly alternating erythrodiisotactic type of stereoregularity. No norbornene blocks are observed.[21] A deep and detailed analysis of these spectra apparently similar reveals significant quantitative differences, which will provide new insights into polymerization mechanisms.

An updated set of assignments of the ^{13}C NMR spectra of alternating erythrodiisotactic E−N copolymers is reported in Table 3. This is the result of the present work, as described in the following sections. Besides the assignments published earlier by us and other authors, Table 3 includes new assignments of $S_{\alpha\beta}$ methylenes of EENENEE, NENENEE, and NENENEN sequences and of the C2/C3 tertiary carbons in NENEE sequences. It was possible to obtain these assignments because a complete analysis of the spectra of copolymers with different norbornene content where the relative peak areas of each spectrum are simultaneously best fitted was carried out (see below). Several of these assignments are in agreement with those reported by other authors.[9,10,22]

As already shown in Table 1 and discussed in ref 17, the methylene region between 27.73 and 28.39 ppm shows a great number of resonances arising from ethylene-centered sequences. These signals correspond to carbons $S_{\delta+\delta+}$, $S_{\delta\delta+}$, $S_{\beta\delta+}$, $S_{\gamma\gamma+}$, $S_{\alpha\delta+}$, $S_{\alpha\delta}$, and $S_{\beta\gamma}$ and give information at the pentad level. Between 28.56 and 28.70 ppm, there are at least four distinct resonances of $S_{\alpha\beta}$ carbons, which partially overlap. Although the origin of such small differences in chemical shifts is not clear, the information here is at heptad level.

The resonance at 28.33 ppm is due to isolated or alternating C5/C6 carbons of sequence ENE: here the information is only at triad level. Peaks at 30.89, 30.96, and 31.04 ppm had already been assigned to C7 carbons.[9,22] Here the differences in chemical shifts are very small; however, they contain information at pentad resolution. Assignments at the pentad level of the C1/C4 signals of isotactic alternating sequences date back to ref 16.

The region of tertiary carbons C2/C3 between 45.09 and 45.78 ppm shows three distinct signals of the four expected at pentad resolution. Previous assignments only distinguished between isolated and alternating signals.[9,27,17] According to our assignments in Table 3, the signal at 45.09 ppm is due to C3 of pentad EENEN, while the signal at 45.78 ppm is due to C2 of EENEN as well as to C2/C3 of NENEN.

Figures 8 and 9 show the spectra of a high N content sample obtained by **2** and of a low N content sample obtained by **3**, respectively. The two figures report the chemical shift(s), the *normalized peak area* (*NPA*), and the sequence(s) associated with each signal (or group of signals). The procedure used to best fit the molar fractions was described in a previous work.[17]

We note that the even ethylene block NEEN (see signals $S_{\alpha\delta}$ and $S_{\beta\gamma}$), which is important to establish the copolymerization mechanism, is observed in both samples.

Worth noting is that although most assignments which provide pentad level information in the spectra of isotactic alternating E−N copolymers had already been identified earlier,[9,10,22] the information contained in the spectra has not been fully exploited up to now, either because of low spectra resolution or because of the peak areas of all the regions of the spectra were not accounted for.

Pentad Microstructure of Alternating E−N Copolymers. Despite the mentioned controversial assignments in the CH_2 region, it may be shown that in the absence of blocks NN (and for simplicity also in the absence of racemic alternating sequences), as is the case of the spectra of E−N copolymer samples in Figures 8 and 9, the current level of assignments allows for the complete determination of the microstructure at the

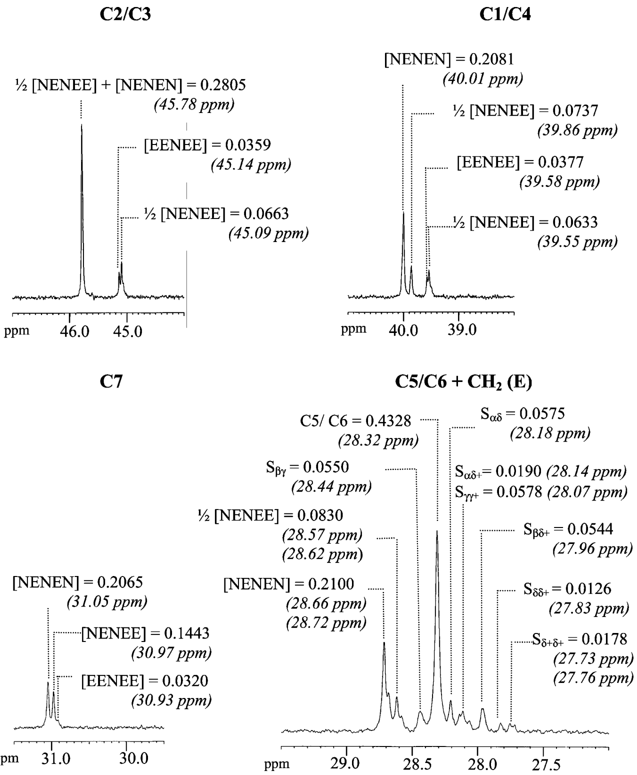


Figure 8. Quantitative analysis of the spectrum of a sample of an E−N copolymer prepared with metallocene **2** with 39.8 mol % of norbornene content (entry no. 17).

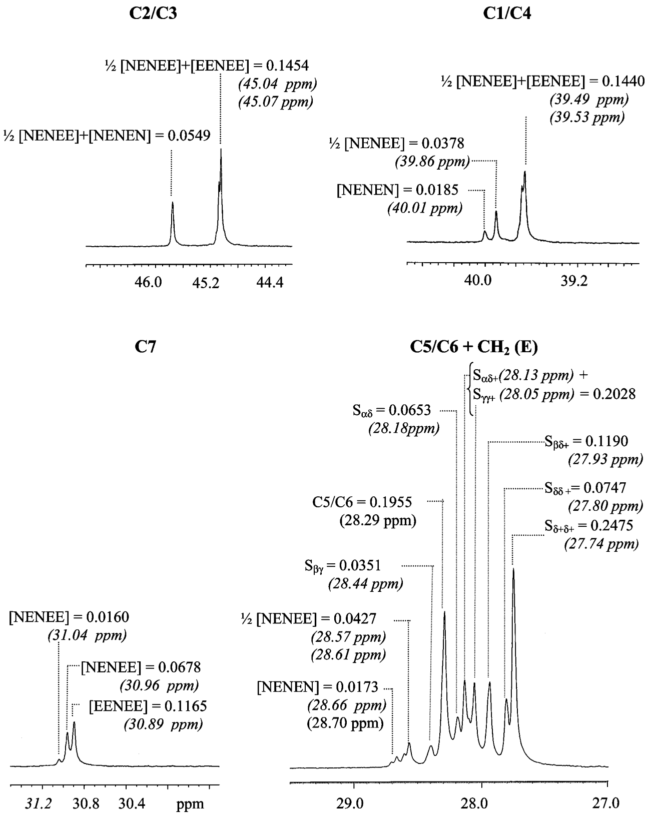


Figure 9. Quantitative analysis of the spectrum of a sample of an E−N copolymer prepared with metallocene **3** with 20.4 mol % of norbornene content (entry no. 5).

pentad level if the information gathered from the whole spectrum is exploited. This fact may result in a more accurate estimate of the copolymerization parameters.

As described above, Figures 8 and 9 report the spectra of two copolymer samples obtained by **2** and **3**, respectively. The two examples are chosen to show how the copolymer microstructure can be derived. The procedure adopted, including the definition of the variables involved, was reported in a previous work;[18] the reader can find the details of the present case in the Appendix.

Here it is sufficient to say that for each area (in some cases more areas) one linear equation relates the NPA to the variables chosen to describe the microstructure in terms of sequence distribution. Least-squares fitting of the set of equations so obtained provides the best solution for the molar fraction of each sequence. According to our current signal assignments, six variables are needed to represent quantitatively the areas of the signals observed in the spectra of the copolymers investigated in this work. In the absence of NN diads, the variables are $f(m)$ = (NEN) = (ENENE); f_0 = (NEEN) = $^1/_2$(NEENE); f_1 = (NEEEN); f(isl) = $^1/_2$(NEE) = $^1/_2$(ENEE); f_E(isl), the total amount of isolated E, i.e., the molar fraction of E units contained in NEE. sequences; and f_N(isot) = (NENEN). Only five variables are independent since f_E(isl) + f(isl) + 2 $f(m)$ = 1 (from normalization); f(isl) is treated as dependent. This number of independent variables, five, corresponds to the number of independent pentads among the nine nonzero ones present in these E−N copolymers. So, a complete description of the copolymer microstructure at pentad level is obtained in the present treatment (see the next section).

Inspection of Figures 8 and 9 shows the high degree of consistency among the various NPAs associated with a given sequence. For example, for copolymer LB228 (entry no. 17) the signals associated with pentad NENEN arising from carbons C1/C4, C7, and ethylene CH_2 have NPA values of 0.208, 0.2065, and 0.210, respectively, while those related to molar fraction $^1/_2$(NENEE) due to carbons C3, C1, C7, and CH_2 of ethylene have NPAs of 0.066, 0.074, 0.072, and 0.083, respectively. The coefficients of the set of equations derived for entry no. 17 are shown in Table 8, for the sake of clarity. We recognize that such equations are not all independent, since the sum of the NPAs related to CH_2 is normalized to 1 and the sums of the NPAs related to C2/C3, C1/C4, and C7 are normalized to f(N). It should be added that the number of equations is not the same for all the samples, depending on the resolution of each spectrum.

The results of the microstructural analysis at pentad level of a number of samples obtained with catalysts **2** and **3** are summarized in Tables 4a and 5a, respectively.

For comparison, the analysis was then repeated at tetrad level (three independent variables), by removing the pentad splittings: (NENEN) + $^1/_2$(NENEE) = $^1/_2$ (NENE) = $f(m)$; (EENEE) + $^1/_2$(NENEE) = $^1/_2$(EENE) = f(isl); and (EEEEE) + $^1/_2$(NEEEE) = $^1/_2$(NEEE) = $f(S\delta^+\delta^+)$ + $f(S\delta\ \delta^+)$.

Only some of these results at the tetrad level are reported for brevity in Tables 4b and 5b.

The microstructure of each sample reported in these tables was first computed on the basis of our current ^{13}C NMR assignments (Table 3), denoted as assignment I. The computations were then repeated (assignment II) by accounting for the different assignments of three signals in the CH_2 region proposed by Fink (see Table 1). The assignments according to Arndt could not be used since they were rather limited, due to the lack of resolution in his spectra. Finally, following our usual

Table 4. Least-Squares Fitting for E−N Copolymer Samples Obtained with Catalyst *i*-Pr(3-Pr^i−Cp)(Flu)ZrCl$_2$ (2)

a. Least-Squares Fitting of Pentad Molar Fractions

entry sample	feed ratio N/E	assgn[a]	R^2 (%)	*f*(N)	EEEEE	NEEEE	NEEEN	ENEEE	NEENE	ENENE	EENEE	NENEE	NENEN
no. 12 LB222	0.282	I	99.996	0.0882	(EEE = 0.7482)			0.1363	0.0146	0.0127	0.0645	0.0219	0.0018
		II	99.996	0.0871	0.6168	0.1245	0.0100	0.1444	0.0048	0.0124	0.0638	0.0216	0.0016
		III	99.997	0.0876	0.6156	0.1271	0.0071	0.1413	0.0085	0.0127	0.0640	0.0218	0.0018
no. 13 LB223	0.430	I	99.990	0.1135	0.5153	0.1634	0.0018	0.1670	0.0182	0.0210	0.0778	0.0294	0.0062
		II	99.990	0.1142	0.5180	0.1478	0.0143	0.1765	0.0065	0.0227	0.0769	0.0292	0.0081
		III	99.990	0.1166	0.5217	0.1442	0.0076	0.1594	0.0270	0.0234	0.0779	0.0307	0.0081
LB224	0.695	I	99.995	0.1577	0.3860	0.1779	0.0014	0.1807	0.0578	0.0384	0.0912	0.0560	0.0104
		II	99.992	0.1560	0.3852	0.1622	0.0226	0.2074	0.0285	0.0380	0.0916	0.0528	0.0116
		III	99.995	0.1572	0.3849	0.1723	0.0093	0.1909	0.0472	0.0388	0.0911	0.0558	0.0102
no. 14 LB225	0.961	I	99.985	0.2154	0.2332	0.1819	0.0118	0.2055	0.0790	0.0731	0.0951	0.0944	0.2590
		II	99.990	0.2136	0.2318	0.1569	0.0431	0.2431	0.0389	0.0726	0.0954	0.0911	0.0270
		III	99.992	0.2141	0.2315	0.1696	0.0299	0.2291	0.0523	0.0732	0.0938	0.0942	0.0261
no. 15 LB226	2.33	I	99.977	0.2404	0.1848	0.1797	0.0098	0.1993	0.0905	0.0955	0.0867	0.1165	0.0372
		II	99.986	0.2395	0.1846	0.1416	0.0490	0.2395	0.0523	0.0936	0.0910	0.1099	0.0387
		III	99.990	0.2393	0.1834	0.1568	0.0376	0.2319	0.0555	0.0955	0.0857	0.1161	0.0375
no. 16 LB227	4.00	I	99.977	0.3120	0.0926	0.1183	0.0218	0.1620	0.1247	0.1687	0.0698	0.1472	0.0951
		II	99.981	0.3081	0.0901	0.0900	0.0631	0.2163	0.0649	0.1675	0.0708	0.1394	0.0978
		III	99.990	0.3095	0.0894	0.1113	0.0396	0.1904	0.0910	0.1688	0.0673	0.1467	0.0954
no. 17 LB228	9.00	I	99.978	0.3980	0.0244	0.0383	0.0303	0.0989	0.1230	0.2870	0.0358	0.1504	0.2119
		II	99.977	0.3938	0.0214	0.0302	0.0525	0.1353	0.0813	0.2856	0.0372	0.1420	0.2146
		III	99.986	0.3945	0.0202	0.0559	0.0277	0.1113	0.1033	0.2872	0.0327	0.1492	0.2126

b. Tetrad Least-Squares Fitting of two E−N Copolymer Samples

entry sample	feed ratio N/E	assgn[a]	R^2 (%)	*f*(N)	EEEE	NEEE	NEEN	ENEE	NENE
no. 16 LB 227	4.00	I	99.844	0.3191	0.1513	0.1579	0.0526	0.2631	0.3751
		II	99.856	0.3112	0.1449	0.2139	0.0187	0.2513	0.3712
		III	99.876	0.3156	0.1463	0.1895	0.0331	0.2557	0.3754
no. 17 LB 228	9.00	I	99.851	0.4041	0.0492	0.0923	0.0504	0.1931	0.6150
		II	99.817	0.3979	0.0450	0.1146	0.0446	0.2038	0.5921
		III	99.864	0.4019	0.0461	0.1115	0.0385	0.1886	0.6152

[a] Three calculations differ in the assignments of three signals in the CH$_2$ region: I, according to Tritto et al.[18]; II, according to Fink et al.[13]; III, intermediate assignment as explained in the text.

Table 5. Least-Squares Fitting for E−N Copolymer Samples Obtained with Catalyst *i*-Pr(3-Me−Cp)(Flu)ZrCl$_2$ (3)

a. Least-Squares Fitting of Pentad Molar Fractions

entry sample	feed ratio N/E	assgn[a]	R^2 (%)	*f*(N)	EEEEE	NEEEE	NEEEN	ENEEE	NEENE	ENENE	EENEE	NENEE	NENEN
no. 4 LB209	0.63	I	99.987	0.015 98	0.3638	0.1716	0.0144	0.2004	0.0608	0.0292	0.1068	0.0475	0.0055
		II	99.986	0.1572	0.3620	0.1646	0.0309	0.2264	0.0295	0.0293	0.1062	0.0436	0.0074
		III	99.989	0.1582	0.3618	0.1748	0.0182	0.2113	0.0463	0.0293	0.1052	0.0472	0.0058
no. 5 LB210	0.92	I	99.994	0.2041	0.2543	0.1631	0.0232	0.2095	0.0929	0.0529	0.1155	0.0715	0.0171
		II	99.997	0.2004	0.2502	0.1433	0.0569	0.2571	0.0405	0.0516	0.1157	0.0661	0.0185
		III	99.999	0.2010	0.2497	0.1628	0.0372	0.2372	0.0594	0.0526	0.1130	0.0708	0.0172
no. 6 LB211	1.36	I	99.990	0.2659	0.1334	0.1393	0.0300	0.1994	0.1313	0.1006	0.1072	0.1162	0.0425
		II	99.980	0.2606	0.1299	0.1273	0.0607	0.2487	0.0732	0.0996	0.1073	0.1074	0.0459
		III	99.995	0.2625	0.1292	0.1517	0.0324	0.2164	0.1070	0.1008	0.1039	0.1156	0.0430
LB212	2.13	I	99.995	0.2909	0.0998	0.1148	0.0368	0.1883	0.1454	0.1240	0.0957	0.1424	0.0529
		II	99.978	0.2839	0.0938	0.1088	0.0644	0.2377	0.0925	0.1188	0.1040	0.1223	0.0576
		III	99.997	0.2871	0.0945	0.1379	0.0313	0.2006	0.1231	0.1253	0.0892	0.1453	0.0527
no. 7 LB213	3.62	I	99.997	0.3564	0.0362	0.0724	0.0310	0.1344	0.1610	0.2087	0.0567	0.1820	0.1176
		II	99.979	0.3493	0.0310	0.0500	0.0722	0.1946	0.1014	0.2014	0.0733	0.1494	0.1267
		III	99.995	0.3523	0.0305	0.0962	0.0254	0.1469	0.1396	0.2090	0.0521	0.1824	0.1178
no. 9 LB215	17.66	I	99.997	0.4050	0.0397	0.0286	0.0174	0.0633	0.1453	0.3007	0.0132	0.1823	0.2095
		II	99.985	0.4003	0.0356	−0.0072	0.0641	0.1209	0.0932	0.2932	0.0278	0.1585	0.2140
		III	99.998	0.4029	0.0362	0.0356	0.0205	0.0766	0.1274	0.3009	0.0103	0.1833	0.2092

b. Tetrad Least-Squares Fitting of Three E−N Copolymer Samples

sample	feed ratio N/E	assgn[a]	R^2 (%)	*f*(N)	EEEE	NEEE	NEEN	ENEE	NENE
no. 5 LB 210	0.92	I	99.975	0.2081	0.3351	0.2077	0.0418	0.2898	0.1263
		II	99.980	0.2017	0.3278	0.2560	0.0127	0.2814	0.1221
		III	99.985	0.2048	0.3298	0.2372	0.0234	0.2839	0.1258
no. 7 LB 213	3.62	I	99.994	0.3570	0.0697	0.1354	0.0809	0.2973	0.4167
		II	99.963	0.3458	0.0614	0.1960	0.0509	0.2977	0.3940
		III	99.995	0.3558	0.0681	0.1459	0.0745	0.2949	0.4167
no. 9 LB 215	17.66	I	99.995	0.4059	0.0502	0.0643	0.0736	0.2115	0.6004
		II	99.975	0.3958	0.0423	0.0197	0.463	0.2124	0.5792
		III	99.997	0.4046	0.0483	0.0763	0.0662	0.2087	0.6005

[a] Three calculations differ in the assignments of three signals in the CH$_2$ region: I, according to Tritto et al.[18]; II, according to Fink et al.[13]; III, intermediate assignment as explained in the text.

Table 6. Comparison between M1, M2, and TSAM (Arndt) Statistical Models of Polymerization with Catalyst 2 from Pentad Level Analysis of ^{13}C NMR Spectra

a. Pentad Level Analysis of ^{13}C NMR Spectra

entry sample	feed ratio N/E	assgn[a]	M1		M2			TSAM	
			r_1	(ese)	r_{11}	r_{21}	(ese)	r_1	(ese)
no. 12 LB222	0.282	I	2.74	0.0079	2.80	1.67	0.0007	1.33	0.0096
		II	2.98	0.0067	3.04	1.69	0.0038	1.44	0.0053
		III	2.86	0.0138	2.92	1.65	0.0144	1.37	0.0049
no. 13 LB223	0.43	I	2.96	0.0110	2.99	2.25	0.0114	1.41	0.0213
		II	2.99	0.0121	3.03	2.13	0.0122	1.42	0.0107
		III	3.04	0.0095	3.11	1.90	0.0055	1.46	0.0192
LB224	0.695	I	3.19	0.0196	3.30	2.19	0.0184	1.54	0.0423
		II	3.19	0.0129	3.27	2.33	0.0103	1.56	0.0224
		III	3.19	0.0132	3.28	2.23	0.0083	1.53	0.0344
no. 14 LB225	0.961	I	2.65	0.0221	2.82	1.93	0.0168	1.32	0.0569
		II	2.69	0.0283	2.84	1.98	0.0274	1.27	0.0310
		III	2.67	0.0216	2.85	1.94	0.0160	1.28	0.0393
no. 15 LB226	2.33	I	5.25	0.0306	5.85	3.61	0.0221	2.67	0.0653
		II	5.36	0.0325	5.89	3.75	0.0277	2.57	0.0354
		III	5.34	0.0309	5.93	3.61	0.0215	2.58	0.0394
no. 16 LB227	4.00	I	4.60	0.0363	6.38	3.41	0.0162	2.65	0.0803
		II	5.26	0.0558	7.22	3.32	0.0392	2.64	0.0392
		III	5.00	0.0428	6.93	3.33	0.0127	2.66	0.0574
no. 17 LB228	9.00	I	3.52	0.0312	7.34	3.41	0.0085	2.51	0.0763
		II	3.89	0.0598	10.18	3.20	0.0302	2.64	0.0486
		III	3.51	0.0437	9.22	3.29	0.0066	2.58	0.0663

b. Tetrad Level Analysis of ^{13}C NMR Spectra

entry sample	feed ratio N/E	assgn[a]	M1		M2			Arndt	
			r_1	(ese)	r_{11}	r_{21}	(ese)	r_1	(ese)
no. 16 LB227	4.00	I	3.64	0.0756	7.10	2.78	0.0114	2.47	0.0696
		II	4.02	0.0958	7.44	2.83	0.0544	2.52	0.0238
		III	3.85	0.0857	7.28	2.78	0.0265	2.48	0.0429
no. 17 LB228	9.00	I	3.17	0.0469	8.82	2.83	0.0044	2.35	0.0663
		II	3.53	0.0539	9.20	3.10	0.0151	2.58	0.0570
		III	3.19	0.0592	9.84	2.77	0.0165	2.37	0.0590

[a] Three calculations differ in the assignments of three signals in the CH_2 region: I, according to Tritto et al.[18]; II, according to Fink et al.[13]; III, intermediate assignment as explained in the text.

trial-and-error method, a careful inspection of the data concerning the three controversial signals led us to consider an intermediate third assignment (III): following Fink,[12] the contribution of $S_{\gamma\delta}$ is moved from peak 4 at 28.07 ppm of Table 1 to peak 6; however, following Tritto,[16,17] the contribution of $S_{\alpha\delta}$ remains at peak 6 and the assignment of peak 9 is unchanged.

Here we would like to outline that assignment III gives nearly always the best fitting. On the average, assignment I gives a better fitting than assignment II, especially in the analysis of copolymers prepared with the methyl-substituted metallocene **3**; assignment II gives a better fitting than I for some of the copolymers prepared by the isopropyl-substituted metallocene **2**. Differences among the molar fractions of pentads are visible in the amounts of NEEEN, ENEEE, and NEENE, that is in those in which the evaluation of the three controversial signals is important.

From these results we can draw the following conclusion: assignment I regarding signals $S_{\alpha\delta}$ and $S_{\alpha\beta}$ is correct, however, as stated by Fink, it appears that signal $S_{\gamma\delta}$ does not overlap to signal $S_{\gamma\delta+}$, but is shifted to lower field.

With regard to the analysis at tetrad level upon the removal of the pentad splittings, in general we find that the fit is less satisfactory than at pentad level. The difference in the quality of fit is especially high in the case of catalyst **2** and also for those samples prepared with catalyst **3** at high N/E feed ratio. This seems to be related to the copolymerization statistics. As we shall see in the following section, the copolymerization can be described by first-order Markov statistics for the samples in which tetrad and pentad fits are similar, while second-order Markov statistics is necessary when fitting differences are significant.

Polymerization Statistics from Copolymer Microstructure. (a) Tetrad Level. The analysis of copolymer microstructure at tetrad level allows one to test both the first-order and the second-order statistics, while triad distributions only allow fitting but not testing the second order Markov model.[19,24] In the past few years, our continuous interest in the investigation of the microstructure of ethylene−norbornene copolymers by combining the use of NMR techniques with computational methods made it possible to achieve assignments and quantification of isolated, alternating, and blocky norbornene sequences, including differentiation between *meso* and *racemic* NEN and ENNE sequences. Recently, our understanding of complex NMR spectra of E−N copolymers yielded complete tetrad sequence distributions.[19] Thus, it was possible to determine the copolymerization parameters and clarify possible statistical models of copolymerization, discriminating between ultimate and penultimate effects. The results on reactivity ratios regarding E−N copolymers obtained with catalysts *rac*-Et(indenyl)$_2$ZrCl$_2$ (**4**), *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$ (**5**), and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**6**) showed that in general better fits are obtained with the second-order Markov statistics which appears to be valid in these cases.[19] Thus, it has been stated that the next-to-last E or N monomer unit exerts an influence on the reactivity of the propagating Mt−E* or Mt−N* species. Such an influence seems to be contingent upon the catalyst structure.

Table 7. Comparison between M1, M2, and TSAM Statistical Models of Polymerization with Catalyst 3

a. Pentad Level Analysis of ^{13}C NMR Spectra

entry sample	feed ratio N/E	assgn[a]	M1		M2			TSAM	
			r_1	(ese)	r_{11}	r_{21}	(ese)	r_1	(ese)
no. 4 LB209	0.63	I	2.69	0.0078	2.69	2.76	0.0093	1.60	0.043 92
		II	2.69	0.0146	2.67	3.00	0.0165	1.28	0.0316
		III	2.69	0.0034	2.68	2.83	0.0035	1.30	0.0383
no. 5 LB210	0.92	I	2.73	0.0124	2.74	2.69	0.0148	1.38	0.0615
		II	2.77	0.0309	2.75	2.92	0.0350	1.32	0.0418
		III	2.75	0.0119	2.75	2.77	0.0138	1.34	0.0465
no. 6 LB211	1.36	I	2.40	0.0129	2.47	2.28	0.0146	1.31	0.0821
		II	2.61	0.0313	2.71	2.32	0.0350	1.29	0.0539
		III	2.51	0.0114	2.61	2.26	0.0099	1.31	0.0711
LB212	2.13	I	3.01	0.0111	3.14	2.86	0.0116	1.72	0.0882
		II	3.40	0.0311	3.57	3.04	0.0344	1.73	0.0627
		III	3.17	0.0154	3.46	2.76	0.0100	1.73	0.0790
no. 7 LB213	3.62	I	2.78	0.0146	3.23	2.60	0.0096	4.60	0.0738
		II	3.25	0.0500	4.39	2.54	0.0442	3.49	0.0626
		III	2.94	0.0286	3.89	2.52	0.0166	1.76	0.0899
no. 9 LB215	17.66	I	6.78	0.0254	9.27	6.72	0.0262	4.60	0.0978
		II	7.21	0.0552	16.10	6.32	0.0424	4.94	0.0606
		III	6.79	0.0311	12.07	6.57	0.0241	4.72	0.0875

b. Tetrad Level Analysis of ^{13}C NMR Spectra

entry sample	feed ratio N/E	assgn[a]	M1		M2			TSAM	
			r_1	(ese)	r_{11}	r_{21}	(ese)	r_1	(ese)
no. 5 LB210	0.92	I	2.69	0.0228	2.84	2.08	0.0122	1.36	0.0590
		II	2.68	0.0346	2.77	2.26	0.0449	1.33	0.0471
		III	2.67	0.0246	2.80	2.15	0.0236	1.34	0.0471
no. 7 LB213	3.62	I	2.71	0.0178	3.30	2.58	0.0089	1.83	0.1053
		II	3.08	0.0470	3.97	2.77	0.0511	1.97	0.0808
		III	2.73	0.0215	3.47	2.56	0.0022	1.83	0.0981
no. 9 LB215	17.66	I	6.59	0.0306	11.54	6.32	0.0325	4.76	0.0959
		II	7.34	0.0523	17.45	6.48	0.0188	5.32	0.0591
		III	6.62	0.0331	13.44	6.18	0.0214	4.80	0.0860

[a] Three calculations differ in the assignments of three signals in the CH_2 region: I according to Tritto et al. (ref 18); II according to Fink et al. (ref 13); III intermediate assignment as explained in the text.

(b) Pentad Level. Here, we shall use the pentad description of the microstructure of the alternating copolymers prepared with catalysts **2** and **3**, reported in Tables 4 and 5, to test different copolymerization mechanisms. The results of such tests are presented in Tables 6 and 7.

Catalysts **2** and **3** are two of the typical catalysts, such as *i*-Pr[(3-R−Cp)(Flu)]ZrCl$_2$ (R = Me, Pr^i, Bu^t), which produce *isotactic alternating* E−N copolymers. They have C_1 symmetry and high steric hindered ligands.[9,10] The analysis of stereoregular alternating E−N copolymers has been used to elucidate polymerization mechanistic details such as the importance of *chain migration mechanism* vs *chain retention mechanism*.[9,12] In the case of a *chain migration mechanism* the monomer insertion occurs alternatively at one or the other coordination site. Norbornene units can be inserted only at the more open coordination site, while the small E can be inserted at both sites. This mechanism should allow only odd ethylene blocks. In the case of *retention mechanism* E and N units are inserted at the same coordination site of the catalysts. This mechanism allows for the formation of odd and even ethylene blocks. Arndt[9] used a statistical model which differentiates two heterotopic sites of the catalyst *i*-Pr[(3-Bu^t−Cp)(Flu)]ZrCl$_2$ (**1**): one site, always in a Zr−E* state, follows first-order Markov statistics; the second one can be in both Zr−E* and Zr−N* states and follows second-order Markov statistics. He concluded that E−N copolymerization follows a chain migration mechanism. On the other hand, Fink et al.[10] have recently analyzed at triad level the E−N copolymer spectra obtained with *i*-Pr[(3-Pr^i−Cp)(Flu)]ZrCl$_2$ (**2**) by using their assignments.[12] They did observe even numbered ethylene sequences and concluded that the microstructure of the copolymer is consistent with *a retention mechanism* rather than with an alternating (switching-site) mechanism. Moreover, from a comparison of the root-mean-square residuals (R values) which correlate experimental and theoretical triad molar fractions calculated according to first-order (M1) and second-order (M2) Markov statistics, they concluded that E−N copolymerization with this catalyst follows first-order Markov statistics.

We have used our pentad level information on these copolymers to test M1 and M2 statistics as well as the two-site alternating mechanism (TSAM) proposed by Arndt. This comparison is based on the experimental pentad molar fractions obtained following the three different sets of assignments, considered in the previous section, of three signals in the CH$_2$ region. An inspection of the fitting estimated standard errors (ese) in Tables 6 and 7 tells us at a first glance that the two-site alternating mechanism is not valid for E−N copolymerization with both catalysts. This result, which holds with all the three assignments, corresponds to the clear evidence of the NEENE sequence in all samples.

Regarding copolymerization statistics, we observe neat differences between the two catalysts. Results clearly indicate that the second-order Markov statistics is more appropriate to describe the series of copolymerizations with catalyst **2**. The r_1 values obtained by us are quite similar to those obtained by Fink et al. and in fact are almost independent from the type of assignment.

This result is especially evident with assignments I and III, while differences between ese values with M1 and M2 are smaller when using Fink's assignment II.

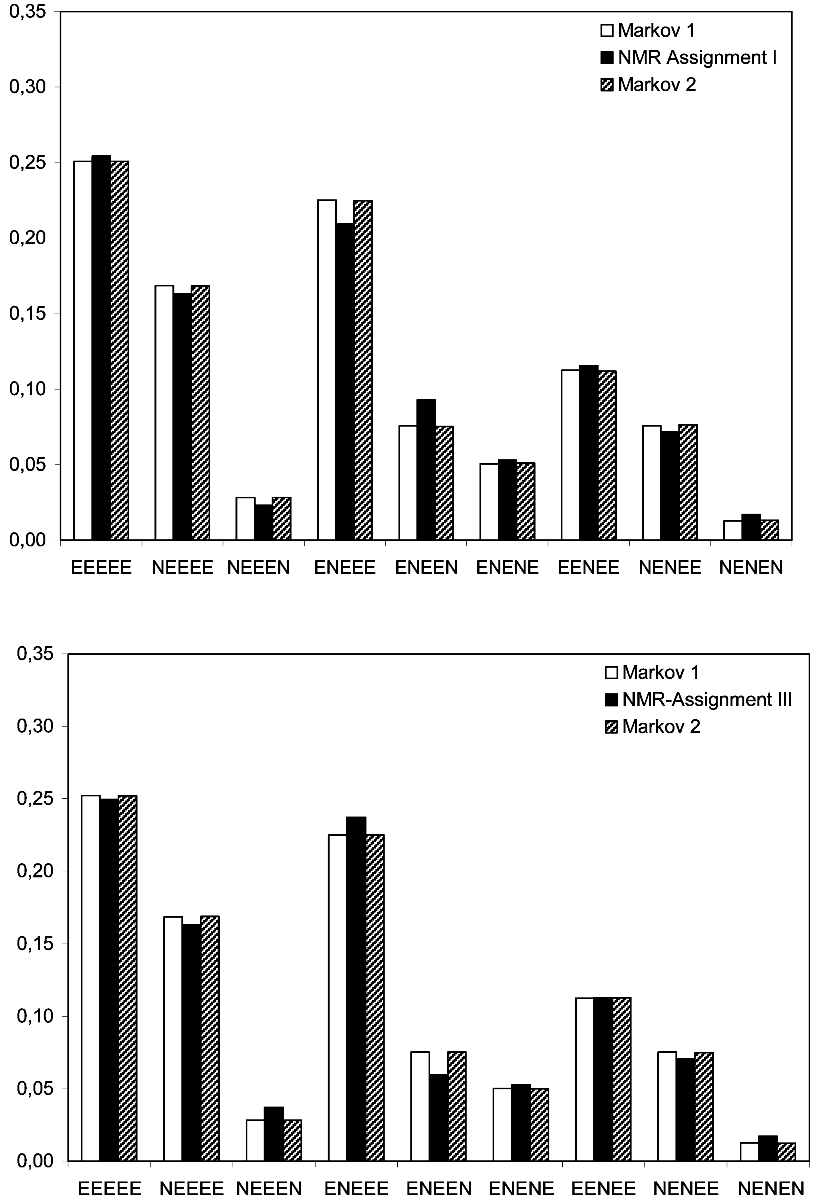


Figure 10. Experimental and calculated pentad distributions for E−N copolymer sample prepared with *i*-Pr(3-Me−Cp)(Flu)-$ZrCl_2$, (**3**) at feed ratio 0.92 (entry no. 5). Key: black, experimental data obtained from NMR with assignments I or III; white, results according to model M1; hatched, results according to model M2.

On the contrary, it turns out that the first-order Markov statistics is sufficient to describe the copolymerization with the Me-substistuted metallocene **3**, at least for copolymers prepared at feed ratios not too high. Indeed, differences in the fitting between M1 and M2 are so small for copolymers prepared by **3** that r_{11} and r_{21} are similar to r_1. This indicates that when Cp is substituted with the small methyl substituent the penultimate inserted unit does not have any influence on the selection of the next unit. This agrees with a previous observation by Kaminsky,[22] who found that E−N copolymerization with the C_s symmetric metallocene *i*-Pr[(Cp)(Flu)]$ZrCl_2$ (**7**) follows first-order Markov statistics. The application of our methodology to analyze E−N copolymer samples obtained with **7** confirms these results. Thus, the methyl Cp substituent behaves similarly to proton.

These features are more evident in Figures 10 and 11, where the NMR-measured pentad distributions obtained by our methodology (with assignments I and III) are compared with those calculated according to first- and second-order Markovian models. One representative copolymer sample produced by **2** and one produced by **3** were selected for such a comparison. Entries nos. 17 and 5 contain 39.8 mol % and 20.4 mol % of norbornene incorporated, respectively.

It is clear that, independently of the assignment used for calculating the experimental NMR pentads: (i) sequences with even ethylene units ENEEN are present in the two copolymers, thus ruling out the two-sites alternating mechanism for E−N copolymerization with these catalysts; (ii) the first-order Markov statistics accurately describes the copolymer sample derived from catalyst **3**; (iii) the second-order Markov statistics is necessary to describe the copolymer microstructure of the copolymer sample produced by **2**; worth noting is the fact that the highest discrepancy between experimental and calculated sequences is found for pentad ENEEN.

Mechanistic Considerations. Polymerization statistics from pentad analysis rules out that the synthesis of isotactic alternating E−N copolymers from C_1-sym-

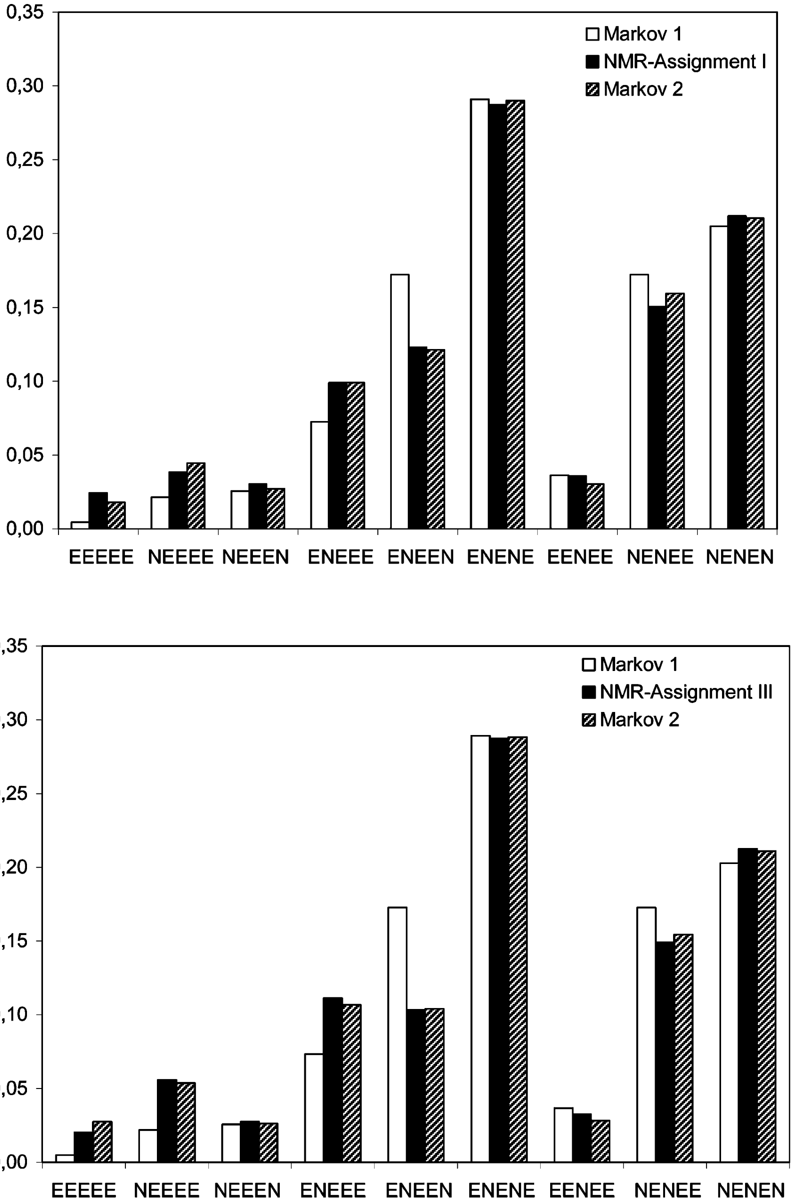


Figure 11. Experimental and calculated pentads distributions for E−N copolymer sample prepared with i-Pr(3-Pr^i−Cp)(Flu)ZrCl$_2$ (**2**) at feed ratio 9.00 (entry no. 17). Key: black, experimental data obtained from NMR with assignments I or III; white, results according to model M1; hatched, results according to model M2.

metric catalysts **2** and **3** can derive from a two-site alternating mechanism. This finding seems to be in contrast with the currently more accepted explanation for the synthesis of isotactic alternating E−P copolymers with the same catalysts. According to this explanation the two sites should have sufficiently different kinetic selectivities toward the two comonomers so that only one of the two comonomers is selected at the more hindered site. The isotacticity of the alternating E−P copolymers should derive from the insertion of propene in the stereoselective site. Waymouth et al.[7] brought indirect evidence for the Cossee-type alternating (switching) site mechanism in which ethylene and propene insert alternately at the two heterotopic sites, although they admit that the single site mechanism cannot be ruled out. They compared stereochemistry and stereoerrors in E−P copolymers with those of the corresponding hemiisotactic propene homopolymer.

The present analysis of the microstructures of isotactic alternating E−N copolymers reveals that the synthesis of the copolymers prepared with both **2** and **3** comes from a retention mechanism, confirming Fink's observation. Thus, these C_1-symmetric catalysts behave as single-site catalysts and both ethylene and norbornene are inserted at the same site, bringing to isotactic NENEN sequences. Here, quite instructive is the comparison with mechanistic evidences obtained by the microstructure of E−N copolymers produced by i-Pr-[(Cp)(Flu)]ZrCl$_2$ (**7**). This catalyst produces copolymers with higher N content and in higher yield than catalysts **2** and **3**; that is, it is possible to obtain copolymers with N content well above 50%. The ENNE sequences present in these copolymers are only *racemic.* This observation is convincing evidence that a Cossee-type mechanism holds also for E−N copolymerizations. Thus, the olefin insertion involves the migration of the polymer chain to the site occupied by the coordinated monomer. This implies that the E−N copolymer chain produced by catalysts **2** and **3**, independent of the last inserted unit, has to skip back to its original site before the next monomer can be inserted at the same site. It seems reasonable that norbornene and ethylene are

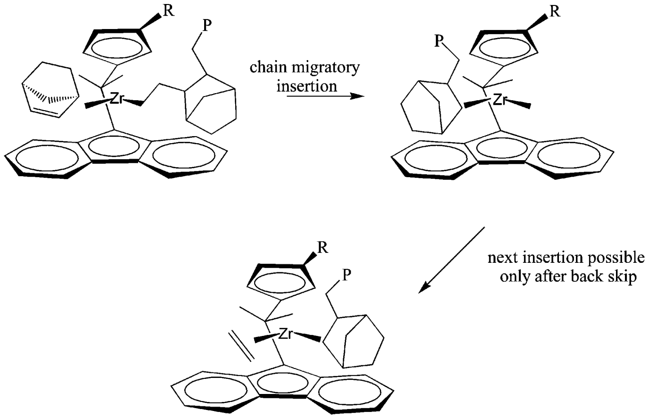


Figure 12. E−N copolymerization mechanism by C_1 metallocenes.

inserted on the more open site following Cossee's migratory mechanism and the copolymer chain after every insertion occasionally skips back to a less stable state, explaining the slow kinetics of E−N copolymerization (Figure 12). The synthesis of alternating E−N copolymers, possible only at very high N/E feed ratios, derives from the impossibility of having two consecutive norbornene insertions. The isotacticity is a consequence of norbornene being inserted always at the same site with the same face.

The series of copolymers obtained by **3** follows the first-order Markov statistics at least when they contain N up to 35 mol %, while the series of copolymers obtained by **2** obeys the second-order Markov statistics.

The steric interactions between the growing polymer chain and the methyl Cp substituent of **3** and the isopropyl Cp substituent of **2** seem to be important to determine the statistics of the two series of copolymerizations: M2 with catalyst **2** having the more sterically hindered isopropyl substituent, M1 with catalyst **3** having the smaller methyl substituent.

Conclusions

The microstructural analysis by ^{13}C NMR of alternating isotactic copolymers synthesized with metallocenes **2** and **3** has been completely obtained at the pentad level thanks to the better quality of recent NMR spectra, achieved by having access to an NMR instrument at higher field, and to the use of our methodology which exploits all the peak areas of the spectra and accounts for the stoichoimetric requirements of the copolymer chain. This methodology has allowed us to reconsider some controversial assignments of ethylene CH_2 signals.

The full exploitation of information contained in the E−N copolymer NMR spectra and the present understanding of these spectra at pentad level has allowed for a more accurate test of the statistical model best describing E−N copolymerization with C_1 symmetric catalysts and to study the influence of ligand substitution of these catalysts on the polymerization mechanism.

We have found that norbornene and ethylene are inserted at the same site by a Cossee's migratory mechanism and a subsequent backskip of the copolymer chain to its original position after every insertion.

The synthesis of alternating E−N copolymers, possible only at very high N/E feed ratios, is a result of the impossibility of having two consecutive norbornene insertions. The isotacticity is a consequence of norbornene being inserted always at the same site with the same face. The steric interactions between the growing polymer chain and the methyl Cp substituent of catalyst **3** and the isopropyl Cp substituent of catalyst **2** seem to be important to determine the copolymerization statistics.

Experimental Part

General Conditions. All experiments were performed under dry nitrogen, in a drybox or using standard Schlenk line techniques. Methylaluminoxane (MAO) (30 wt % as toluene solution, Witco) was dried (50 °C, 3 h, 0.1 mmHg) before use. Toluene was dried and distilled from sodium under nitrogen atmosphere. *i*-Pr(3-Me−Cp)(Flu)$ZrCl_2$ was purchased from Boulder and *i*-Pr(3-Pr^i−Cp)(Flu)$ZrCl_2$ from Mcat-Gmbh. Ethylene was dried on $CaCl_2$ and molecular sieves. Oxygen was removed by fluxing the gas through BTS catalysts. Norbornene was distilled from sodium and used as stock solution in toluene.

Polymer Synthesis. A typical ethylene−norbornene copolymerization experiment with metallocenes **2** and **3** was performed at 30 °C in a 250 mL round-bottomed Schlenk flask. After 3 vacuum−nitrogen cycles, norbornene was introduced in the reactor. Toluene (100 mL) was then cannula transferred, and MAO was added as a toluene solution ([Al] = 3 mol·L^{-1}). After evacuation of the nitrogen, the solution was saturated with ethylene at atmospheric pressure. The reacting medium was stirred for 30 min in order to dissolve the ethylene and to homogenize the medium. The catalyst was then added as a toluene solution (typically [Zr] = 0.010 mmol·L^{-1}, Al/Zr = 3000). The pressure of ethylene was kept constant during the polymerization. Copolymerization reactions were stopped before the medium would become heterogeneous and before 10% of the initially introduced norbornene was consumed. At the end of the reaction, the reaction mixture was poured into acidic ethanol. The precipitated polymer was washed with EtOH and dried under vacuum.

Ethylene concentration in toluene was calculated according to Henry's law, as already described.[18]

Ethylene was used instead of nitrogen to purge the Schlenk flask before introducing the reagents.

^{13}C NMR Characterization. The copolymers were dissolved in $C_2D_2Cl_4$. HMDS was used as internal reference. Analyses were performed at 103 °C on a Bruker AV-400 spectrometer in the PFT mode. Composite pulse decoupling was used to remove ^{13}C−^{1}H couplings.

The norbornene content of the copolymers was calculated according to the formula $[2I(C_7) + I(C_1{-}C_2) + I(C_2{-}C_3)] \times 100/3I(CH_2)$, where $I(CH_2)$, $I(C_7)$, $I(C_1{-}C_2)$, and $I(C_2{-}C_3)$ are the peak areas in the ranges 26−30, 30−36, 34−42, and 43−54 ppm of ^{13}C NMR spectra as previously reported.[20]

Calculation of Pentad Distribution and Reactivity Ratios. The pentad distributions were calculated from the segment molar fractions: $f(m)$, f_0, f_1, $f(\mathrm{isl})$, $f_E(\mathrm{isl})$, as defined in ref 17, and $f_N(\mathrm{isot})$, which represents pentad NENEN.

For comparison, the analysis was then repeated at tetrad level (three independent variables), by removing the pentad splittings: (NENEN) + $^1/_2$(NENEE) = $^1/_2$(NENE) = $f(m)$; (EENEE) + $^1/_2$(NENEE) = $^1/_2$(EENE) = $f(isl)$;and (EEEEE) + $^1/_2$ (NEEEE) = $^1/_2$ (NEEE) = $f(S\ \delta^+\delta^+) + f(S\ \delta\ \delta^+)$. The determination of the copolymerization parameters is described in the Appendix.

Acknowledgment. This work is dedicated to Prof. Adolfo Zambelli, whose scientific originality and openmindedness we have always heartily admired. We thank Mr. G. Zannoni for his valuable cooperation in NMR analysis.

Appendix I

Tables 8 and 9 are given, showing pentad level least-squares fittings of normalized peak areas of samples LB228 and LB210.

Table 8. Pentad Level Least-Squared Fitting of Normalized Peak Areas of Sample LB228 (Entry No. 17) of E−N Alternating Copolymer[a]

		normalized peak area							
LB228	carbon	obsd	calcd	$E(m)$	f_0	f_1	f(isl)	f_E(isl)	N isot
f(N)		0.3828	0.3970	1	0	0	1	0	0
$f(\delta^+\delta^+)$	CH_2−E	0.0178	0.2437	0	2	1	−4	1	0
$f(\delta\ \delta^+)$	CH_2−E	0.0126	0.0192	0	−1	−1	1	0	0
$f(\beta\ \delta^+)$	CH_2−E	0.0544	0.0495	0	−1	0	1	0	0
$f(\gamma\ \gamma^+)$	CH_2−E	0.0190	0.0494	0	−1	0	1	0	0
$f(\alpha\ \delta^+)$	CH_2−E	0.0578	0.0494	0	−1	0	1	0	0
$f(\alpha\ \delta)$	CH_2−E	0.0575	0.0615	0	1	0	0	0	0
ENE	C5/C6	0.4328	0.3980	1	0	0	1	0	0
$f(\beta\ \gamma)$	CH_2−E	0.0550	0.0615	0	1	0	0	0	0
½NENEE	CH_2−E	0.0830	0.0752	1	0	0	0	0	−1
NENEN	CH_2−E	0.2100	0.2119	0	0	0	0	0	1
EENEE	C7	0.0320	0.0358	−1	0	0	1	0	1
NENEE	C7	0.1443	0.1504	2	0	0	0	0	−2
NENEN	C7	0.2065	0.2119	0	0	0	0	0	1
EENEE + ½NENEE	C1/C4	0.1011	0.1110	0	0	0	1	0	0
½NENEE	C1	0.0737	0.0752	1	0	0	0	0	−1
NENEN	C1/C4	0.2081	0.2118	0	0	0	0	0	1
½NENEE	C3	0.0663	0.0752	1	0	0	0	0	−1
EENEE	C2/C3	0.0359	0.0358	−1	0	0	1	0	1
½NENEE + NENEN	C2/C3	0.2805	0.2870	1	0	0	0	0	0
				0.2870[b]	0.0615	0.0303	0.1110	0.31494	0.2118
				0.0062[c]	0.0075	0.0156		0.0165	0.0067

av length of isolated sequences = 2.84
$R^2 = 99.978$

[a] Columns 5−10 Represent the Coefficients of Each Variable of the Set of Equations. [b] Best fitting molar fraction. [c] Deviation.

Table 9. Pentad Level Least-Squared Fitting of Normalized Peak Areas of Sample LB210 (Entry No. 5) of E−N Alternating Copolymer

		normalized peak area							
LB210	carbon	obsd	calcd	$E(m)$	f_0	f_1	f(isl)	f_E(isl)	N isot
f(N)		0.2003	0.2041	1	0	0	1	0	0
$f(\delta^+\delta^+)$	CH_2−E	0.2475	0.2543	0	2	1	−4	1	0
$f(\delta\ \delta^+)$	CH_2−E	0.0747	0.0816	0	−1	−1	1	0	0
$f(\beta\ \delta^+)$	CH_2−E	0.1190	0.1048	0	−1	0	1	0	0
$f(\gamma\ \gamma^+) + f(\alpha\ \delta^+)$	CH_2−E	0.2028	0.2095	0	−2	0	2	0	0
$f(\alpha\ \delta)$	CH_2−E	0.0653	0.0464	0	1	0	0	0	0
ENE	C5/C6	0.1955	0.2041	1	0	0	1	0	0
$f(\beta\ \gamma)$	CH_2−E	0.0351	0.0464	0	1	0	0	0	0
1/2 NENEE	CH_2−E	0.0427	0.0357	1	0	0	0	0	−1
NENEN	CH_2−E	0.0173	0.0171	0	0	0	0	0	1
EENEE	C7	0.1165	0.1155	−1	0	0	1	0	1
NENEE	C7	0.0678	0.0715	2	0	0	0	0	−2
NENEN	C7	0.0160	0.0171	0	0	0	0	0	1
EENEE + ½NENEE	C1/C4	0.1440	0.1512	0	0	0	1	0	0
½NENEE	C1	0.0378	0.0357	1	0	0	0	0	−1
NENEN	C1/C4	0.0185	0.0171	0	0	0	0	0	1
EENEE	C2/C3	0.1454	0.1512	0	0	0	1	0	0
NENEE + NENEN	C2/C3	0.0549	0.0526	1	0	0	0	0	0
				0.0529[b]	0.0465	0.0232	0.1121	0.7431	0.01711
				0.003 98[c]	0.0043	0.0092		0.0066	0.0041

av length of isolated sequences = 4.91
$R^2 = 99.994$

[a] Columns 5−10 represent the coefficients of each variable of the set of equations. [b] Best fitting molar fraction. [c] Deviation.

Appendix II: Determination of the Copolymerization Parameters of Isotactic Alternating Copolymers

The pentad level microstructures of the E−N copolymers presented in this work were analyzed according to the first-order and second-order Markovian statistical models by means of the procedure described below. The reader is referred to previous work(17) for details concerning the determination of the molar fractions of the chain segments, $f(m)$, f_0, f_1, f(isl), f_E(isl), and f_N(isot), and consequently of the pentad molar fractions F(pentad) $\equiv F^0{}_k$. These quantities ($F^0{}_{ki}$ for sample i) are treated here as the *experimental* pentad molar fractions. In the following, well-known general equations of copolymerization statistics[24] are applied to the specific case of E−N copolymers at pentad level.

First-Order Markov. The copolymerization parameter r_1 is defined and related to the probabilities P (P_{lm} is the probability that monomer m is inserted in a bond l−metal) by

$$r_1 = k_{EE}/k_{EN} = (1/P_{EN} - 1)f \qquad \text{(A1)}$$

where f is the monomer feed ratio [N]/[E].

Table 10 gives the pentad molar fractions F_k calculated as functions of the first-order probabilities P_{lm} and of the copolymer molar fractions of the two components f_E and f_N. We note that $f_E + f_N = 1$ and that, under the postulated steady-state conditions, $f_E/f_N = P_{NE}/P_{EN}$.

Table 10. Pentad Distribution for an Alternating E−N Copolymer Expressed by Means of the First-Order Markovian Probabilities

(1) $F(\mathrm{EEEEE}) = f_E(1 - P_{EN})^4$
(2) $F(\mathrm{NEEEE}) = 2 f_E P_{EN}(1 - P_{EN})^3$
(3) $F(\mathrm{NEEEN}) = f_N P_{EN}(1 - P_{EN})^2$
(4) $F(\mathrm{ENEEE}) = 2 f_E P_{EN}(1 - P_{EN})^2$
(5) $F(\mathrm{ENEEN}) = 2 f_E P_{EN}{}^2(1 - P_{EN})$
(6) $F(\mathrm{ENENE}) = f_E P_{EN}{}^2$
(7) $F(\mathrm{NENEE}) = 2 f_E P_{EN}{}^2(1 - P_{EN})$
(8) $F(\mathrm{EENEE}) = f_E P_{EN}(1 - P_{NE})2$
(9) $F(\mathrm{NENEN}) = f_N P_{EN}2$

Table 11. Pentad Distribution for an Alternating E−N Copolymer Expressed by Means of the Second-Order Markovian Probabilities

(1) $F(\mathrm{EEEEE}) = f_{EE}(1 - P_{EEN})^3$
(2) $F(\mathrm{NEEEE}) = f_{NE}P_{NEE}(1 - P_{EEN})^2$
(3) $F(\mathrm{NEEEN}) = {}^1/_2\, f_{NE}P_{EEN}P_{NEE}\,(1 - P_{EEN})$
(4) $F(\mathrm{ENEEE}) = f_{NE}P_{NEE}(1 - P_{EEN})$
(5) $F(\mathrm{ENEEN}) = f_{NE}P_{NEE}P_{EEN}$
(6) $F(\mathrm{ENENE}) = {}^1/_2\, f_{NE}(1 - P_{EEN})$
(7) $F(\mathrm{NENEE}) = 2f_{EE}P_{EEN}(1 - P_{NEE})$
(8) $F(\mathrm{EENEE}) = f_{NE}P_{EEN}P_{NEE}$
(9) $F(\mathrm{NENEN}) = {}^1/_2\, f_{NE}(1 - P_{NEE})^2$

Second-Order Markov. In this case the two copolymerization parameters r_{11} and r_{21} are defined and related to the probabilities P (here P_{lmn} is the probability that monomer n is inserted in a bond lm−metal) by

$$r_{11} = k_{EEE}/k_{EEN} = (1/P_{EEN} - 1)f$$
$$r_{21} = k_{NEE}/k_{NEN} = (1/P_{NEN} - 1)f \tag{A2}$$

Table 11 shows the pentad molar fractions F_k calculated as functions of the second-order probabilities P_{lmn} and of the copolymer diad fractions f_{EE} and f_{EN}. One can show that here the following relationships hold:

$$f_{EN} = 1/[1 + {}^1/_2\,(P_{NEE}/P_{EEN})]$$
$$f_{EE} = {}^1/_2\, f_{EN}P_{NEE}/P_{EEN} \tag{A3}$$

With both models, the probabilities P are best-fitted to the experimental pentad fractions by expressing the total discrepancy function Δ

$$\Delta = \Sigma_i\, \Sigma_k\, (F_k - F^0{}_{ki})^2 \tag{A4}$$

(where the sums over i and k are extended to the available samples and to the 9 pentads, respectively), as a function of one or two parameters P, utilizing the expressions of Table 10 or 11, respectively. Minimization of Δ by an iterative procedure provides the solution for the P's; hence, the copolymerization parameters r_i or r_{ij} are computed from eqs A1 or A2, respectively.

Supporting Information Available: Figures showing quantitative analysis of the ^{13}C NMR spectra of samples LB225, LB 226, and LB 227 (entry nos. 14, 15, and 16, respectively) showing the chemical shift(s), the peak area, the assignment, and the molar fraction of sequence(s) associated with each signal (or group of signals). This material is available free of charge via the Internet at http://pubs.acs.org.

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