616 *Macromolecules* **2002,** *35,* 616−623

Ethylene−Norbornene Copolymers from Metallocene-Based Catalysts: Microstructure at Tetrad Level and Reactivity Ratios

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Received July 30, 2001; Revised Manuscript Received October 23, 2001

ABSTRACT: Ethylene−norbornene (E−N) copolymers were synthesized by catalytic systems composed of racemic isospecific metallocene or a constrained geometry catalyst (CGC) and methylaluminoxane. The following metallocenes were used: *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**), *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$ (**2**), *rac*-Me$_2$Si(2-Me-[*e*]-benzindenyl)$_2$ZrCl$_2$ (**3**), and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**4**). The copolymers were characterized by ^{13}C NMR and the copolymer microstructures were analyzed in detail. A procedure for computing the molar fractions of the stereosequences that completely define the microstructure of an E−N copolymer at tetrad level, distinguishing between *meso* and *racemic* contributions to alternating and block sequences, was utilized. The information was converted into the complete tetrad distribution, which allowed us to determine the reactivity ratios, testing the first-order and the second-order Markov statistics. Here, examples of such an use of tetrad description of copolymers to test possible statistical models of copolymerization are given. The first-order r_1 and r_2 reactivity ratios of copolymers prepared with all catalysts depend on the monomer concentration. The products r_1r_2 were found in the range between 0 and 0.177. The tendency to alternate ethylene and norbornene is **4** > **3** > **1** > **2**. The root-mean-square deviations between experimental and calculated tetrads demonstrate that penultimate (second-order Markov) effects play a decisive role in E−N copolymerizations. Our first results show clues for more complex effects depending on the catalyst geometry in copolymers obtained at high N/E feed ratios.

Introduction

Among the attractive features of the metallocene-based catalysts[1] is their ability to give ethylene-based copolymers of uniform composition[2] and to incorporate cycloolefins into the polyethylene backbone.[3] Ethylene−norbornene (E−N) copolymers obtained with metallocene-based catalysts display interesting properties such as high glass transition temperatures, excellent transparency, and good heat/chemical resistance.[4] These copolymer characteristics depend on several parameters, such as the comonomer composition, the distribution of comonomers within the chain, and also the chain stereoregularity. Metallocene structure is the key for producing a controlled copolymer microstructure. In turn, a detailed knowledge of the effectiveness of catalysts in producing a given polymer structure can be achieved provided that a methodology for the detailed determination of the polymer microstructure is available.

High-resolution ^{13}C NMR is one of the most useful methods for studying copolymer composition and microstructure. Several research groups have contributed to the assignment (still incomplete) of the rather complex ^{13}C NMR spectra of E−N copolymers.[5−9]

Progress in chemical shift assignments of these copolymers spectra has included the discrimination of *meso/racemic* relationships between norbornene units in alternating NEN and in ENNE sequences.[5] A further trial-and-error extension of the assignment of unknown signals has been obtained by means of a procedure for computing the molar fractions of the stereosequences that define the microstructure of an E−N copolymer.[5g]

In this contribution, we report on the conversion of such computed molar fractions into the complete conventional description of the copolymer chain in terms of tetrads and on their use to derive the copolymerization parameters. The availability of tetrad information allows us to test both the first-order and the second-order Markov statistics, while triad distribution could allow only fitting of second-order Markov models.[10] Penultimate effects (second-order Markov statistics) have been suggested to play a decisive role in E−N copolymerizations obtained with different metallocene catalysts; see, e.g., refs 6a, 8b, and 11.

The microstructural characterization by ^{13}C NMR analysis of E−N copolymers prepared with four different catalyst precursors, namely *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**), *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$ (**2**), *rac*-Me$_2$Si(2-Me-[*e*]-benzindenyl)$_2$ZrCl$_2$ (**3**), and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**4**), will be reported. **1**−**3** are *C*$_2$-symmetric racemic zirconocenes with *ansa*-bis(indenyl) ligands. **1** has been selected as a reference since it is now considered a benchmark metallocene. **2** and **3** differ from **1** in the type of bridge (−CH$_2$CH$_2$−, Me$_2$Si<). **3** differs from **2** in indenyl substitution (Chart 1).

We have already shown that the indenyl substitution in **3** allows this catalyst to produce mainly isotactic alternating E−N copolymers.[5g,9] The constrained geometry catalyst **4** also yields mainly alternating E−N copolymers, which in this case contain both *meso* and *racemic* NEN sequences. We shall show the calculated tetrad distributions and copolymerization parameters, and present possible statistical models of copolymerization.

Results and Discussion

Complete Tetrad Description of E−N Copolymers. The above-mentioned procedure for analyzing the ^{13}C NMR spectra of E−N copolymers is based on an appropriate partitioning of the molecular chain into

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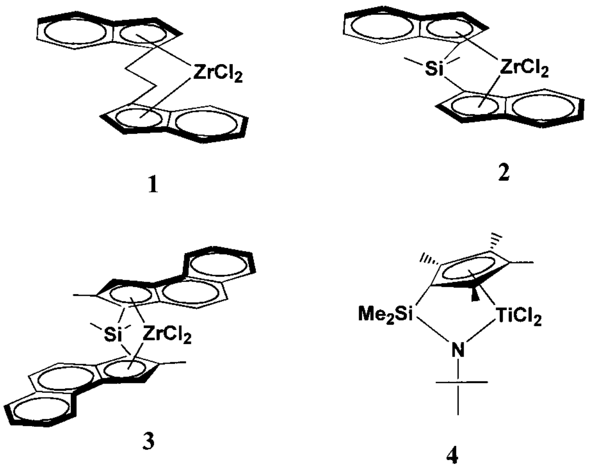
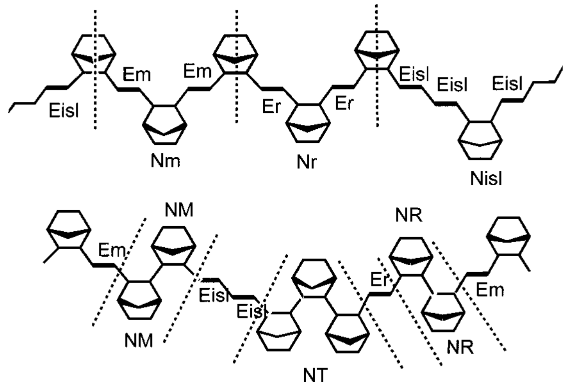
10.1021/ma011365m CCC: $22.00

Chart 1



1 **2** **3** **4**

Scheme 1. Definitions of Segments Used for the Calculations of Molar Fractions



fragments, defined according to the assignment level. Scheme 1 illustrates the various types of chain fragments (isolated, alternating and blocks) defined in the calculation,[5g] which also distinguishes between *meso (m)* and *racemic* (*r*) alternating units and between *meso (M)* and *racemic* (*R*) ENNE sequences.

The molar fractions of such fragments represent one way for describing the chain microstructure: the observed peak areas of the greatest possible number of ^{13}C NMR signals assignable (on the basis of a list of known chemical shifts, such as Table 1 in ref 5g, and of additional hypotheses) are utilized in a computer program[5g] to generate a set of linear equations where the molar fractions are the variables. In summary, for a given spectrum we write a linear equation from each distinctly measured peak area:

$$\text{normalized peak area} = \sum_i c_i f_i$$

where c_i = coefficients and f_i = unknown molar fractions = variables.

The stoichiometric requirements of the chain are accounted for by means of further relationships among the variables. See ref 5g and 9 for a more precise definition of the variables. The least-squares fitting of the set of equations provides the best solution for the unknowns.

The molar fractions of the segments of E−N polymer chain, f_N(isl), f_E(isl), f_0, $f_N(m)$, $f_N(r)$, $f_N(M)$, $f_N(R)$, f_N(block), etc., displayed in Scheme 1 can be estimated with a standard deviation on the order of 1−2%.

Figure 1 shows how the difference in microstructure of E−N copolymers can be illustrated using this technique.[9] The two stereoregular and stereoirregular alternating E−N copolymers, having roughly the same incorporated norbornene content, were obtained with *rac*-Me$_2$Si(2-Me-[*e*]-benzindenyl)$_2$ZrCl$_2$ (**3**) and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**4**), respectively. In particular, quantitative differences in tacticity between the two copolymers are evidenced.

This analysis corresponds to a complete description of the polymer microstructure at tetrad level, besides providing some information at higher level. Indeed, it is possible to express the molar fractions of tetrads as functions of the above variables, as shown by the following equations (eqs 1−10):

$$F(\text{EEEE}) = [f_E(\text{isl}) - 3f(\text{isl}) + f_0] = [f(\delta^+\delta^+) + f(\delta\delta^+)] \tag{1}$$

$$F(\text{NEEE}) = 2\,[f(\text{isl}) - f_0] \tag{2}$$

$$F(\text{NEEN}) = f_0 \tag{3}$$

$$F(\text{ENEE}) = 2f_N(\text{isl}) \tag{4}$$

$$F(\text{NNEE}) = 2[f(\text{isl}) - f_N(\text{isl})] \tag{5}$$

$$F(\text{NENE}) = 2f_N(\text{alt}) = 2[f_N(m) + f_N(r)] \tag{6}$$

$$F(\text{NNEN}) = 2[f(\text{alt}) - f_N(\text{alt})] \tag{7}$$

$$F(\text{ENNE}) = f(\text{diad}) = {}^1\!/_2[f_N(M) + f_N(R)] \tag{8}$$

$$F(\text{NNNE}) = 2\,f(\text{block}) \tag{9}$$

$$F(\text{NNNN}) = f_N(\text{block}) - 3f(\text{block}) \tag{10}$$

We can also distinguish between *meso* and *racemic* contributions to NENE, NNEE, NNEN, and ENNE sequences. We note that NN diads ($f_N(M) + f_N(R)$) are evaluated separately from blocks (NNN and higher blocks). The microstructure as well as the tacticity of the two alternating copolymers are displayed in Figure 2, where the total ethylene and norbornene amounts have been broken into molar fractions of tetrad sequences.

The tetrad description allows for an easy visualization of the copolymer chain, the highly alternating monomer distribution of the copolymers being more evident in Figure 2 than in Figure 1. Such a description evidences and quantifies also the different *meso* and *racemic* NENE contents in the copolymers prepared with catalysts **3** and **4**. As we have already reported elsewhere,[5f,9] the isotacticity of the alternating copolymer obtained with **3** (*rac*-Me$_2$Si(2-Me-[*e*]-benzindenyl)$_2$ZrCl$_2$) is due to its C_2 symmetry. However, the typical feature of all the copolymers prepared with catalyst **3** and with norbornene content above 40 mol % is that they are blockier than the alternating copolymers containing *meso* and *racemic* NEN sequences obtained with **4**. In addition, as clear from Figure 2, their content in NNNE, that is in triad norbornene homosequences, is surprisingly

Table 1. Experimental Tetrad Distributions by ^{13}C NMR of E−N Copolymers Obtained with Different Metallocenes (Mt)[a]

Mt	feed ratio [N]/[E]	% N in the feed	activity[b]	time (min)	N convn (%)	% N in the polym	tetrad									
							EEEE	NEEE	NEEN	ENEE	NNEE	NENE	NNEN	ENNE	NNNE	NNNN
1	2.33	70	$6.64 \times 10^{3\,c}$	1.5	3.5	32.67	0.1251	0.1603	0.0776	0.2988	0.0168	0.2886	0.0163	0.0165	0.0000	0.0000
	3.98	80	$4.60 \times 10^{3\,c}$	2.5	2.7	40.16	0.0546	0.1076	0.0746	0.2300	0.0268	0.4175	0.0488	0.0356	0.0045	0.0000
2	2.33	70	$0.58 \times 10^{3\,d}$	20	4.5	33.68	0.1253	0.1632	0.0756	0.2825	0.0318	0.2552	0.0287	0.0229	0.0148	0.0000
	3.98	80	$0.33 \times 10^{3\,d}$	30	2.8	40.41	0.0715	0.1290	0.0646	0.2070	0.0512	0.3234	0.0798	0.0577	0.0158	0.0000
3	2.33	70	$0.55 \times 10^{3\,d}$	30	4.0	29.63	0.1609	0.1718	0.0826	0.3325	0.0045	0.2366	0.0032	0.0000	0.0079	0.0000
	9.74	90	$0.10 \times 10^{3\,d}$	40	1.0	40.34	0.0553	0.0780	0.0774	0.2260	0.0068	0.5232	0.0157	0.0048	0.0128	0.0000
4	2.33	70	$1.39 \times 10^{3\,c}$	5	2.4	27.42	0.1548	0.2145	0.0822	0.3789	0	0.1696	0	0	0	0
	3.99	80	$1.83 \times 10^{3\,c}$	5	2.0	31.74	0.0796	0.1769	0.1086	0.3941	0	0.2408	0	0	0	0

[a] [Zr] = 0.010 mmol L^{-1}; [Al]/[Zr] = 3000; P_E = 1 atm; T = 30 °C; solvent = toluene. [b] Activity = kg of copolymer/(mol of Mt × h). [c] See Experimental Section. [d] Metallocenes were prealkylated before addition to reaction medium (see Experimental Section).

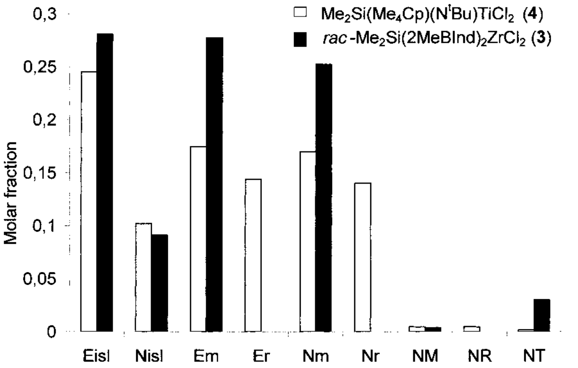


Figure 1. Molar fractions of norbornene and ethylene in different sequence types, defined as reported in ref 5e, and calculated for two copolymer samples prepared with *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**) and $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**) containing 44.1 and 43.6 N mol %, respectively. Key (see Scheme 1): Eisl, f_E(isl); Nisl, f_N(isl); Em, $f(m)$; Nm, $f_N(m)$; NM, $f_N(M)$; NT, f_N(triad) or f_N(block).

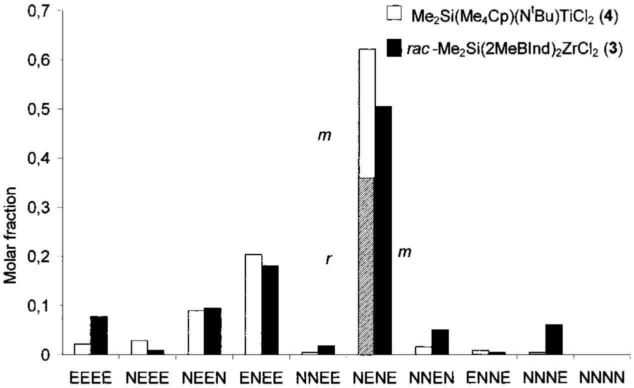


Figure 2. Molar fractions of tetrads, defined from eqs 1−10 and calculated for two copolymer samples prepared with *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**) and $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**) containing 44.1 and 43.6 N mol %, respectively.

greater than the mol % of norbornene in ENNE, that is in norbornene diads.

Determination of the Copolymerization Parameters from Tetrad Analysis

Tetrad Molar Fractions. With the ultimate purpose of examining the influence of catalyst structure on the ethylene/norbornene copolymer microstructures, E−N copolymerizations were carried out with zirconocenes **1-4** activated with methylaluminoxane in toluene at 30 °C in the presence of 10 μmol/L metallocenes. High N/E feed ratios were used to prepare copolymers with high norbornene content, thus allowing us to better evaluate differences in copolymer microstructures. Possible penultimate effects would be more easily detected at high feed ratios. Polymerization yields of the four catalytic systems have been included only for sake of completeness in Table 1. Polymerization tests have been designed to ensure the low comonomer conversion and low polymerization content in the polymerization medium required for the study of the copolymer microstructure rather than to investigate the polymerization activity. Copolymerization tests with catalysts **2** and **3** were performed under slightly different conditions, e.g., the prealkylation of the metallocenes, with respect to those with catalysts **1** and **4**. These factors have no effect on the copolymer microstructure, but they do influence the catalytic efficiency. A thorough comparison of the catalytic efficiency could be made only considering series of data for each catalyst. In general, from these and other results[5f] it is possible to state that the 2-methyl and benz[*e*]indenyl substitution of **3** reduced the catalyst activity with respect to that of **2**. In agreement with other authors, **1** is more active in E−N copolymerization than **2**[3a] and then **4**.[3h]

The copolymer tetrad distributions were estimated using the above method by ^{13}C NMR spectroscopy. The results obtained at two different monomer feed ratios are reported in Table 1. The norbornene content in the copolymers ranges from 27.4 to 40.4 mol %. The zirconocenes **1** and **2**, differing in the type of bridge, yield copolymers with almost equal norbornene content. Catalyst **3**, which differs from **2** in having hindered ligand substitution, allows for a lower norbornene incorporation in the copolymers. The two catalysts **3** and **4**, which produce mainly alternating copolymers (Figures 1 and 2), incorporate rather similar norbornene amounts. Variations in tetrad distributions are most significant. In all the copolymers under study the NNNN value found experimentally is zero. Especially worth noting are changes in distributions of the tetrads representing *isolated* [ENEE = $2f_N$(isl)] and *alternating* [NENE = $2f_N$(alt)] norbornene units and of those of *norbornene blocks* (ENNE, and NNNE). ENEE is at a maximum in the copolymers prepared by the constrained geometry **4** and the methyl-substituted benzindenyl zirconocene **3**, up to 38% and 33%, respectively, while the dimethylsilyl-bridged zirconocene **2** produced a copolymer with the minimum ENEE value. At low feed ratio NENE increases in the order **4** < **3** < **2** < **1**, but it reaches 52% in the copolymer prepared with catalyst **3** at the high feed ratio of 9.74. Very interesting are also differences in ENNE and in NNNE tetrads of copolymers obtained with the indenyl-metallocenes **1**, **2**, and **3**, their percentages being the greatest in the copolymer obtained with **2**, which has a more open *wedge* with respect to **1** and a lower steric hindrance

Table 2. Reactivity Ratios and Tetrad Distributions of E−N Copolymers Calculated Using a First-Order Markov Model[a]

	reacivity ratios						tetrad									
metallocene	feed ratio [N]/[E]	% N in the polym	r_1	r_2	$r_1 \times r_2$	fit[b]	EEEE	NEEE	NEEN	ENEE	NNEE	NENE	NNEN	ENNE	NNNE	NNNN
rac-Et(Ind)$_2$ZrCl$_2$	2.33	33.45	2.602	0.0275	0.072	0.0111	0.0977	0.1750	0.0784	0.3117	0.0200	0.2791	0.0179	0.0178	0.0023	0.0001
(**1**)	3.98	41.43	2.338	0.0309	0.072	0.0101	0.0297	0.1011	0.0860	0.2431	0.0299	0.4139	0.0509	0.0360	0.0089	0.0005
rac-Me$_2$Si(Ind)$_2$ZrCl$_2$	2.33	33.94	2.717	0.0525	0.143	0.0095	0.1049	0.1776	0.0752	0.2927	0.0353	0.2477	0.0299	0.0293	0.0070	0.0004
(**2**)	3.98	41.99	2.871	0.0618	0.177	0.0137	0.0427	0.1184	0.0820	0.2267	0.0557	0.3143	0.0773	0.0534	0.0263	0.0032
rac-Me$_2$Si(2MeBInd)$_2$ZrCl$_2$	2.33	29.47	3.338	0.0071	0.024	0.0118	0.1441	0.2011	0.0702	0.3359	0.0055	0.2345	0.0039	0.0046	0.0002	0.0000
(**3**)	9.74	41.65	4.477	0.0043	0.019	0.0141	0.0182	0.0793	0.0862	0.2416	0.0102	0.5255	0.0222	0.0155	0.0013	0.0000
Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$	2.33	27.20	3.906	0	0	0.0265[c]	0.1789	0.2134	0.0637	0.3408	0	0.2032	0	0	0	0
(**4**)	3.98	30.77	4.988	0	0	0.0362[c]	0.1187	0.1899	0.0760	0.3419	0	0.2735	0	0	0	0

[a] [Zr] = 0.010 mmol L^{-1}; [Al]/[Zr] = 3000; P_E = 1 atm; T = 30 °C; solvent = toluene. [b] Defined as root-mean-square deviation between computed and experimental tetrad fractions [fit = $(\Delta/10)^{1/2}$]. [c] Here the sum of eq A4 is extended to the five nonzero experimental tetrads (see Table 1).

Table 3. Reactivity Ratios and Tetrad Distributions of E−N Copolymers Calculated Using a Second-Order Markov Model[a]

	reacivity ratios							tetrad									
metallocene	feed ratio [N]/[E]	% N in the polym	r_{11}	r_{12}	r_{21}	r_{22}	fit[b]	EEEE	NEEE	NEEN	ENEE	NNEE	NENE	NNEN	ENNE	NNNE	NNNN
rac-Et(Ind)$_2$ZrCl$_2$	2.33	36.23	3.048	0.0247	2.386	0.0081	0.0070	0.1164	0.1779	0.0680	0.2969	0.0171	0.2899	0.0167	0.0165	0.0006	0.0000
(**1**)	3.98	40.38	3.241	0.0298	2.191	0.0176	0.0037	0.0471	0.1156	0.0709	0.2302	0.0273	0.4182	0.0496	0.0359	0.0050	0.0002
rac-Me$_2$Si(Ind)$_2$ZrCl$_2$	2.33	33.85	3.046	0.0489	2.519	0.1393	0.0060	0.1178	0.1779	0.0672	0.2806	0.0316	0.2562	0.0288	0.0229	0.0147	0.0023
(**2**)	3.98	40.52	4.174	0.0622	2.543	0.0339	0.0013	0.0692	0.1320	0.0629	0.2067	0.0511	0.3236	0.0800	0.0578	0.0156	0.0011
rac-Me$_2$Si(2MeBInd)$_2$ZrCl$_2$	2.33	29.72	3.486	0.0061	3.207	0.6179	0.0110	0.1493	0.1995	0.0667	0.3281	0.0047	0.2384	0.0034	0.0017	0.0048	0.0034
(**3**)	9.74	41.18	6.805	0.0035	4.211	0.0809	0.0096	0.0337	0.0965	0.0691	0.2269	0.0078	0.5249	0.0180	0.0072	0.0114	0.0045
Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$	2.33	27.20	3.232	0	5.184	0	0.0029[c]	0.1525	0.2199	0.0792	0.3784	0	0.1700	0	0	0	0
(**4**)	3.98	31.79	3.376	0	6.521	0	0.0024[c]	0.0765	0.1808	0.1068	0.3945	0	0.2414	0	0	0	0

[a] [Zr] = 0.010 mmol L^{-1}; [Al]/[Zr] = 3000; P_E = 1 atm; T = 30 °C; solvent = toluene. [b] Defined as root-mean-square deviation between computed and experimental tetrad fractions [fit = $(\Delta/10)^{1/2}$]. [c] Here the sum of eq A4 is extended to the five nonzero experimental tetrads (see Table 1).

with respect to **3**. We have already commented on the relatively high NNN content in the copolymers obtained with **3**.

Reactivity Ratios. The complete tetrad data of Table 1 allow one to identify the statistical model most suitable to describe the copolymerizations as well as to derive the reactivity ratios between the two comonomers. When the insertion of a comonomer is influenced by the last inserted unit[12] the first-order Markov is sufficient and the following two reactivity ratios are defined

$$r_1 = k_{11}/k_{12} = k_{\mathrm{EE}}/k_{\mathrm{EN}}$$

and

$$r_2 = k_{22}/k_{21} = k_{\mathrm{NN}}/k_{\mathrm{NE}}$$

where k_{mn} represents the rate constant for the insertion of monomer n into an m-metal-ended chain.

When the insertion of a comonomer is influenced by the penultimate unit, then the second-order Markov statistical model is needed to describe the copolymerization and four reactivity ratios are defined:

$$r_{11} = k_{111}/k_{112} = k_{\mathrm{EEE}}/k_{\mathrm{EEN}}$$

and

$$r_{22} = k_{222}/k_{221} = k_{\mathrm{NNN}}/k_{\mathrm{NNE}}$$

as well as

$$r_{21} = k_{211}/k_{212} = k_{\mathrm{NEE}}/k_{\mathrm{NEN}}$$

and

$$r_{12} = k_{122}/k_{121} = k_{\mathrm{ENN}}/k_{\mathrm{ENE}}$$

where k_{lmn} represents the rate constant for the insertion of monomer n into an lm-metal-ended chain.

When using the experimental triad or tetrad distributions to fit the copolymerization equations for first and second-order Markov statistics and to calculate the copolymerization parameters, better fits are always obtained from the second-order Markov model owing to the greater number of parameters, but the meaningfulness of the improvement must be verified.[2a] According to Bovey[10] a triad distribution[8b] does not allow one to test a second-order model. In contrast, the available tetrad information should allow us to test both the first-order and the second-order Markov statistics.

Both models were applied to fit the experimental tetrad distributions of Table 1. The theoretical tetrad distributions and the reactivity ratios were calculated using a statistical approach based on pure Markovian copolymerization models (Tables 2 and 3), as described in the Appendix. To examine the dependence of the copolymerization parameters on the feed ratio, the data of each sample were fitted separately.

The first results on r_1 and r_2 reactivity ratios regarding two samples per catalyst are summarized in Table 2. A general observation on the reported r_1 and r_2 is that the values of r_1 and r_1r_2 are comparable to those observed for other ethylene-based copolymers obtained by metallocenes with low reactivity ratios.[2] The ranges of the reactivity ratios obtained at the lowest N/E feed ratio are as follows: $r_1 = 2.34-4.99$ and $r_2 = 0.0-0.062$. These values are within the same range of those for ethylene–norbornene copolymers, reported in the literature, obtained with the Finemann and Ross method, for which a terminal copolymerization model has to be valid.[3b,e,h,12] The r_2 values are in general smaller than those obtained for propene copolymerization. Large r_1 values in general indicate the preference for the insertion of ethylene over norbornene into Mt–E* (Mt = metallocene) center, while small k_{22} values show the low homopolymerization rate of norbornene. The highest r_1r_2 values found for the copolymers prepared with catalyst **2** confirm its tendency to give more random copolymers. The values of r_1, r_2, and r_1r_2 for the E–N copolymers obtained with catalysts **4** and **3** are comparable with those of alternating ethene-propene copolymers with metallocene catalysts.[2b]

It is worth observing the difference in copolymerization parameters obtained under different monomer feed ratios. Such differences, along with the accuracy of these values as well as the rather high rms deviations shown in Table 2, suggest already that the type of penultimate unit is indeed important in E/N copolymerization. It is worth recalling that such an effect was not observed for ethene-1-octene copolymerization with catalysts **2** and **3**. In addition, the reactivity ratios found were also considerably different: $r_{\mathrm{E}} = 18.9$ and $r_{\mathrm{o}} = 0.014$ (**2**) and $r_{\mathrm{E}} = 10.1$ and $r_{\mathrm{o}} = 0.118$ (**3**).[13]

Such indications are confirmed by inspection of Table 3, where the results of the second-order Markov model are reported. As r_1, also all r_{11} values are similar to those found for ethene and propene copolymerization with metallocene catalysts with low reactivity ratios.[2] Differences in r_{12} and in r_{22} are illuminating, since they clearly show the preference of the insertion of E or N into E–N–Mt and N–N–Mt, respectively. Parameter r_{12} increases in the order **4** < **3** ≪ **1** < **2**, opposite to the tendency to alternate the two comonomers.[14]

The r_{22} values are in general lower than those obtained for propene or other α-olefins, in agreement with the low homopolymerization activity of norbornene. The r_{22} value for catalyst **3** is much greater than r_{12}; this shows the tendency of this catalyst to insert a third norbornene after the second one. All the parameters obtained for the copolymers prepared with **2** are rather close to those reported for ethylene-propene copolymerization ($r_{11} = 4.1$, $r_{21} = 3.9$, $r_{12} = 0.065$, and $r_{22} = 0.153$ at 25 °C).[11] In addition, the four copolymerization parameters calculated for the copolymers prepared with **1** and **4** are quite independent of monomer concentrations, while those for copolymers obtained with **2** and **3** at two different monomer concentrations are quite different.

The experimental tetrad distributions and those calculated according to first- and second-order Markovian models are compared in Figure 3. These comparisons and the rms deviations in Tables 2 and 3 help us to discriminate between first- and second-order Markov models. Worthy of note is the very good agreement between all the calculated with the second-order model and experimental tetrads—*isolated* (ENEE), *alternating* (NENE), and *block* (NNEN, ENNE, NNNE)—in copolymers from **1**, **2**, and **4**.[15] In contrast, the rms values for the alternating copolymers produced from **3** are not satisfactory either with first-order or with second-order models. This appears to confirm our previous hypothesis that various mechanisms are at work with this catalyst.[9,] Finally, it is worth noting that our first results indicate that r_{11}, r_{12}, r_{21}, and r_{22} can be dependent on

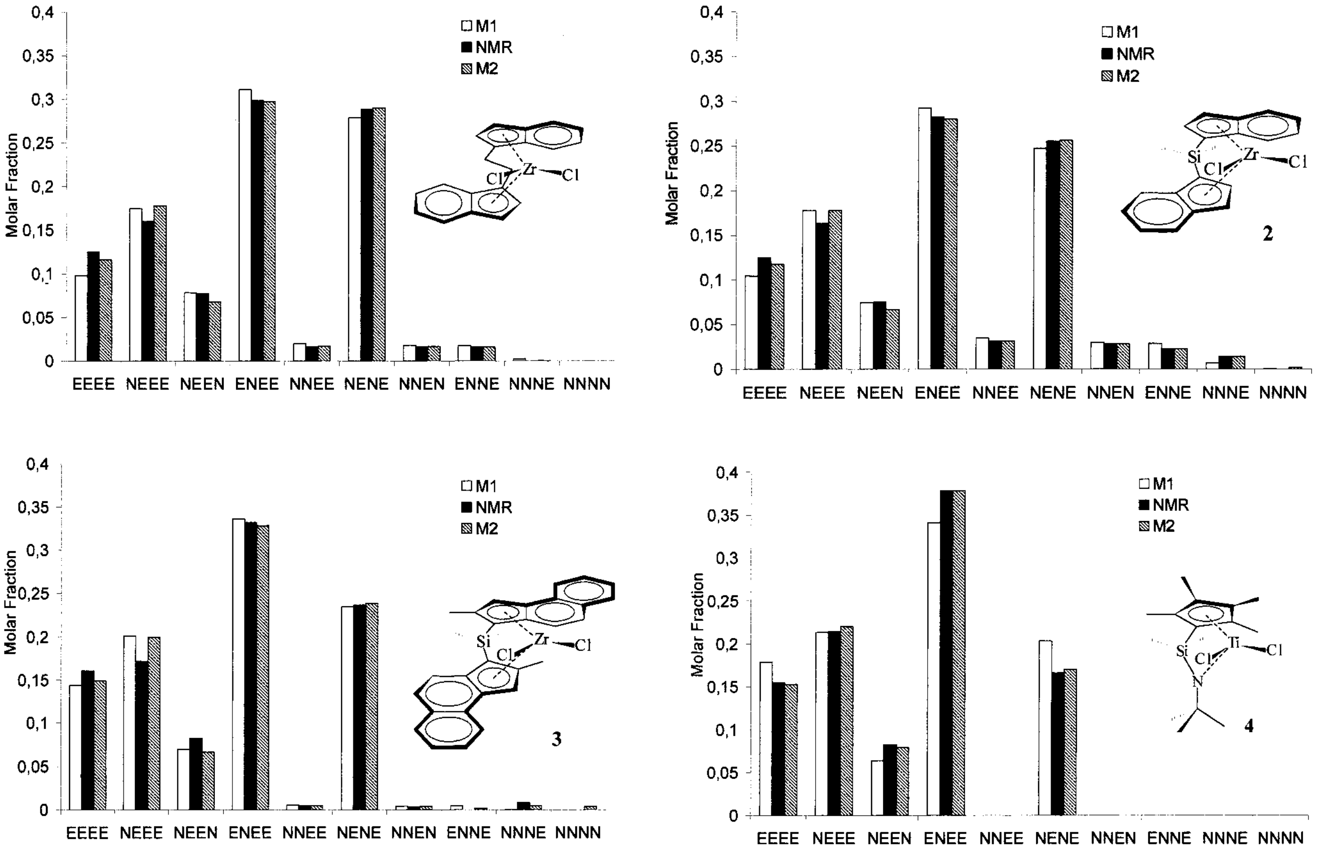


Figure 3. Tetrads distributions for E/N copolymers, and calculated for copolymer samples prepared with *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**), *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$ (**2**), *rac*-Me$_2$Si(2-Me-[*e*]-benzindenyl)$_2$ZrCl$_2$ (**3**) and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (**4**) at feed ratio 2.33. Key: black, experimental data; white, data according to first-order Markov model; shaded, data according to second-order Markov model.[15]

the feed composition, suggesting that at high N/E ratio the reactivity of the propagating species can be influenced by effects more distant than the penultimate monomer unit.

Conclusions

In conclusion, our approach provides a complete description of the copolymer microstructure at tetrad level, with a few indications at higher level, with a standard deviation of 1−2%. Such an accuracy allows one to clarify the statistics of these copolymerizations and to discriminate between ultimate and penultimate effects. At the present stage, it is already possible to state that 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. The second-order Markov model must be used to describe E−N copolymerizations promoted by metallocenes **1**, **2**, and **4**. A third-order model or a more complex model may be required to fit the experimental data obtained with catalyst **3** where more sterically hindered indene substitutions are dominant. At higher norbornene concentrations, copolymers with all catalysts may need more complex models.

Although a large number of data on various catalysts are yet to be analyzed, the present results are sufficient to conceive that E−N copolymerization is dominated by the bulkiness of the norbornene monomer and of the copolymer chain. Extension of this methodology to series of E−N copolymers with a wide range of norbornene content will allow us to definitely select the best statistical model to describe E/N copolymerization with a given catalyst. This will lead to deeper insights into the mechanism of these copolymerizations.

Experimental Section

General Conditions. All experiments were performed under dry nitrogen, in a drybox or using standard Schlenk line techniques. 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. *rac*-Et(indenyl)$_2$ZrCl$_2$ and *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$ were purchased from Witco. Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ was purchased from Boulder. *rac*-Me$_2$Si(2-Me-[*e*]-benzindenyl)$_2$ZrCl$_2$ was synthesized as part of the TMR network in the group of Prof. Brintzinger (Konstanz, Germany). 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 vacuu*m*-nitrogen cycles, norbornene was introduced in the reactor. Toluene (100 mL) was then cannula transferred, and the methylaluminoxane (MAO) was added as a toluene solution ([Al] = 1.74 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). Metallocenes **2** and **3** were prealkylated (Al/Zr = 10) before their addition to reaction medium. The pressure of ethylene was kept constant during the polymerization. Copolymerization reactions were stopped before the medium would become heterogeneous, and before 5% 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.[9]

A similar procedure was used in copolymerization experiments with **1** and **4** where different conditions were the following: (a) **1** and **4** were not prealkylated before their addition to the copolymerization medium; (b) 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. Analysis were performed at 103 °C on a Bruker AM-270 spectrometer at 67.89 MHz 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 the ^{13}C NMR spectra as previously reported.

Calculation of Tetrad Distribution and Reactivity Ratios. The tetrad distribution were calculated from eqs 1−10 from the molar fractions of the segments: Eisl, f_E(isl); Nisl, f_N(isl); Em, $f(m)$; Nm, $f_N(m)$; NM, $f_N(M)$; NT, and f_N(triad) or f_N(block). These are defined in Scheme 1 as described in ref 5g. The determination of the copolymerization parameters is described in the Appendix.

Acknowledgment. We thank Mr. G. Zannoni for his valuable cooperation in NMR analysis. K.T. also thanks the Norwegian Research Council (NFR) for financial support. Financial support from EC TMR Project Network No. ERB FMRX CT97-0116 GLASSCYCLICS is gratefully acknowledged.

Appendix: Determination of the Copolymerization Parameters

The tetrad-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[5g] for details concerning the determination of the molar fractions of the segments of the chain f_N(isl), f_E(isl), f_0, f_N(m), f_N(r), f_N(M), f_N(R), f_N(block), etc. and consequently of the tetrad molar fractions F(tetrad) = $F^0{}_k$, defined and numbered according to eqs 1−10 of the text. These quantities ($F^0{}_{ki}$ for sample i) are treated here as the *experimental* tetrad molar fractions. In the following, well-known general equations of copolymerization statistics[11] are applied to the specific case of E−N copolymers at the tetrad level.

First-Order Markov. The copolymerization parameters r_i are defined and related to the probabilities $\boldsymbol{P}$ (P_{lm} is the probability that monomer m is inserted in a bond l−metal) by the equations

$$r_1 = k_{EE}/k_{EN} = (1/P_{EN} - 1)f; \quad r_2 = k_{NN}/k_{NE} = (1/P_{NE} - 1)/f \quad \text{(A1)}$$

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

Table 4 gives the tetrad 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 4. Tetrad Distribution for an E−N Copolymer Expressed by Means of the First-Order Markovian Probabilities

(1) $F(\mathrm{EEEE}) = f_E(1 - P_{EN})^3$
(2) $F(\mathrm{NEEE}) = 2f_EP_{EN}(1 - P_{EN})^2$
(3) $F(\mathrm{NEEN}) = f_NP_{NE}P_{EN}(1 - P_{EN})$
(4) $F(\mathrm{ENEE}) = 2f_EP_{NE}P_{EN}(1 - P_{EN})$
(5) $F(\mathrm{NEEN}) = 2f_EP_{EN}(1 - P_{NE})(1 - P_{EN})$
(6) $F(\mathrm{NENE}) = 2f_EP_{EN}{}^2P_{NE}$
(7) $F(\mathrm{NENN}) = 2f_NP_{NE}P_{EN}(1 - P_{NE})$
(8) $F(\mathrm{ENNE}) = f_EP_{NE}P_{EN}(1 - P_{NE})$
(9) $F(\mathrm{NNNE}) = 2f_NP_{NE}(1 - P_{NE})^2$
(10) $F(\mathrm{NNNN}) = f_N(1 - P_{NE})^3$

Table 5. Tetrad Distribution for an E−N Copolymer Expressed by Means of the Second-Order Markovian Probabilities

(1) $F(\mathrm{EEEE}) = f_{EE}(1 - P_{EEN})^2$
(2) $F(\mathrm{NEEE}) = f_{NE}P_{NEE}(1 - P_{EEN})$
(3) $F(\mathrm{NEEN}) = {}^1/_2\, f_{NE}P_{NEE}P_{EEN}$
(4) $F(\mathrm{ENEE}) = f_{NE}P_{NEE}(1 - P_{ENN})$
(5) $F(\mathrm{NEEN}) = 2f_{EE}P_{EEN}P_{ENN}$
(6) $F(\mathrm{NENE}) = f_{NE}(1 - P_{NEE})(1 - P_{ENN})$
(7) $F(\mathrm{NENN}) = f_{NE}P_{ENN}(1 - P_{NEE})$
(8) $F(\mathrm{ENNE}) = {}^1/_2\, f_{NE}P_{NNE}P_{ENN}$
(9) $F(\mathrm{NNNE}) = f_{NE}P_{ENN}(1 - P_{NNE})$
(10) $F(\mathrm{NNNN}) = f_{NN}(1 - P_{NNE})^2$

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

$$r_{11} = k_{EEE}/k_{EEN} = (1/P_{EEN} - 1)f; \quad r_{22} = k_{NNN}/k_{NNE} = (1/P_{NNE} - 1)/f$$

$$r_{21} = k_{NEE}/k_{NEN} = (1/P_{NEN} - 1)f; \quad r_{12} = k_{ENN}/k_{ENE} = (1/P_{ENE} - 1)/f \quad \text{(A2)}$$

Table 5 shows the tetrad molar fractions F_k calculated as functions of the second-order probabilities P_{lmn} and of the copolymer diad fractions f_{EE}, f_{EN}, and f_{NN}. One can show that here the following relationships hold:

$$f_{EN} = 1/[1 + {}^1/_2(P_{NEE}/P_{EEN} + P_{ENN}/P_{NNE})];$$

$$f_{EE} = {}^1/_2\, f_{EN}P_{NEE}/P_{EEN};\ f_{NN} = {}^1/_2\, f_{EN}P_{ENN}/P_{NNE} \quad \text{(A3)}$$

With both models, the probabilities $\boldsymbol{P}$ are best-fitted to the experimental tetrad fractions by expressing the total discrepancy function Δ

$$\Delta = \sum\nolimits_i \sum\nolimits_k (F_k - F^0{}_{ki})^2 \quad \text{(A4)}$$

(where the sums over i and k are extended to the available samples and to the 10 tetrads, respectively), as a function of the two or four parameters $\boldsymbol{P}$, utilizing the expressions of Table 4 or 5, respectively. Minimization of Δ by an iterative procedure provides the solution for the $\boldsymbol{P}$'s; hence, the copolymerization parameters r_i or r_{ij} are computed from eqs A1 or A2, respectively.

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(14) The high tendency of **4** to produce alternating copolymers, shown in Figures 1 and 2 and in ref 9, does not appear in Tables 1−3 because NENE also depends on the feed ratio f = [N]/[E]. A useful expression in this regard is $F(NENE) = F(NE)/(1 + r_{12} f + r_{21}/f + r_{12}r_{21})$.

(15) In Figure 3, the discrepancies between experimental and second-order molar fractions mainly concern the three EE-centered tetrads (EEEE, NEEE, and also NEEN). A possible reason could be that signals of such tetrads appear only in the region between 27 and 30 ppm, which is overcrowded in the ^{13}C NMR spectra of copolymers containing high norbornene content, while the other tetrads can be calculated from signals of C1−C4, C2−C3, and C5−C6.

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