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Stereoregular and Stereoirregular Alternating Ethylene−Norbornene Copolymers

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ABSTRACT: Ethylene−norbornene (E−N) copolymers were synthesized with the C_2 metallocene *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**) and with the constrained geometry $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**) in the presence of methylaluminoxane. The E−N copolymerizations were carried out using a variety of monomer feed compositions. Copolymers were fully characterized by ^{13}C NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. Copolymer microstructures were analyzed in detail, through a procedure which accounts for the stoichiometric requirements of the copolymer chain as well as for the measured areas of ^{13}C NMR signals. This analysis, which quantifies the differences in sequence distribution and tacticity of the polymers, evidenced that mainly alternating stereoregular and stereoirregular copolymers were prepared with **3** and **4,** respectively. The copolymer prepared with **4** contains both *meso* and *racemic* NEN sequences and small amounts of *meso* and *racemic* NN diads, while the alternating copolymer prepared with **3** contains only *meso* NEN sequences and small amounts of *meso* NN diads. The formation of NN diads is disfavored with both catalysts. Surprisingly, a significant amount of norbornene (up to ∼10%) belonging to NNN triads (*T*) is obtained with the C_2 catalyst.

Introduction

The newly developed metallocene-based catalysts for olefin polymerization have some unique characteristics.[1] Among them is their capability of polymerizing cyclic olefins via addition without ring-opening metathesis[2] as well as yielding ethylene-based copolymers with new microstructures.[3] Ethylene−norbornene (E−N) copolymers synthesized using metallocene catalysts have interesting properties such as high glass transition temperatures and transparency.[4−6] Moreover, with respect to norbornene homopolymers prepared in the presence of the same catalysts, they have the great advantage of being processable. Copolymer properties depend on many parameters, such as the comonomer composition, the distribution of comonomers within the chain, and also the chain stereoregularity, which are determined by the structure of the catalyst precursor. The design of E−N-based materials with given features requires a detailed description of the microstructure of copolymers as well as a complete understanding of the relationships between the microstructure and the material properties.

However, because of the complexity of their ^{13}C NMR spectra, a description of these copolymers as well as a detailed understanding of the processes and mechanisms involved in these copolymerizations proved difficult to be achieved. This explains the great interest directed in the past few years toward the determination of the comonomer composition and distribution along the E−N copolymer chain by ^{13}C NMR spectroscopy.[7−10] Differences in stereoregularity of norbornene sequences, which need to be taken into account, make the spectra even more complex and have been overlooked even in the case of the simplest alternating E−N copolymers. Indeed, the configuration at C2/C3 carbon atoms of two successive norbornene units, obtained from *cis*-2,3-*exo* insertion, can be either *S*/*R* or *R*/*S*, that is *meso* or *racemic,* and a perfectly alternating E−N copolymer can be either *isotactic* or *syndiotactic.* The existence and the origin of differences in the ^{13}C NMR spectra arising from *meso*/*racemic* sequences were recently demonstrated (Figure 1).[7e]

The synthesis of perfectly alternating ethylene−norbornene copolymers was first disclosed by Cherdron.[4a] Subsequently, alternating ethylene−norbornene copolymers have been reported to have been synthesized with the C_1-symmetric, bridged metallocenes $R_2C(Flu)(3\text{-}R'Cp)ZrCl_2$ [R = Me or Ph, R′ = Me or *tert*-butyl] (**1**),[10a] in the presence of an excess of norbornene, and with group 4 bridged monocyclopentadienyl catalysts such as μ-Me_2Si(3-*tert*-butyl cyclopentadienyl) (adamantylamido)MMe_2 [M = Zr, **2a**, or Hf, **2b**] (Figure 2).[11] Recently C_1-symmetric, bridged metallocenes and monocyclopentadienyl titanium amido complexes different from those reported above have also been shown to yield mainly alternating ethylene−norbornene copolymers.[12]

Scheme 1 shows a proposed mechanism of alternating ethylene−norbornene copolymerization.[10a] As discussed later in greater detail, the alternating structure of the copolymers should result from the more crowded catalytic site being accessible only by ethylene, while the great excess of norbornene favors its insertion at the more open site.

In this study, the synthesis of two series of different alternating ethylene−norbornene copolymers obtained with *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**) and $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**), respectively, will be reported.

We have recently developed a procedure for computing the molar fractions of the stereosequences which define the microstructure of an E−N copolymer, utiliz-

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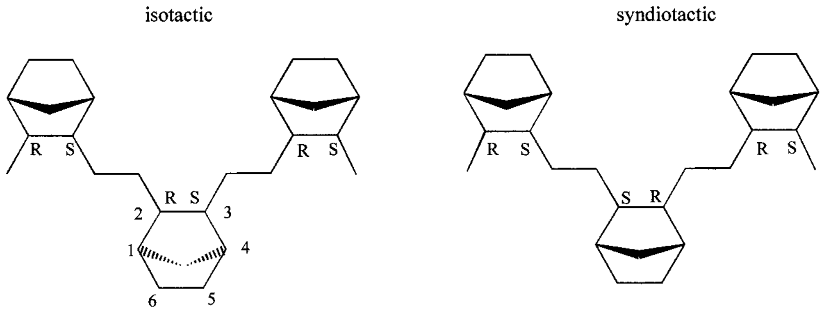


Figure 1. Segments of isotactic and syndiotactic alternating ethylene–norbornene copolymers.

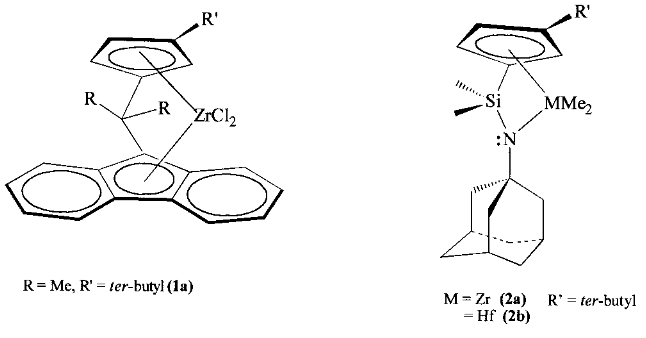
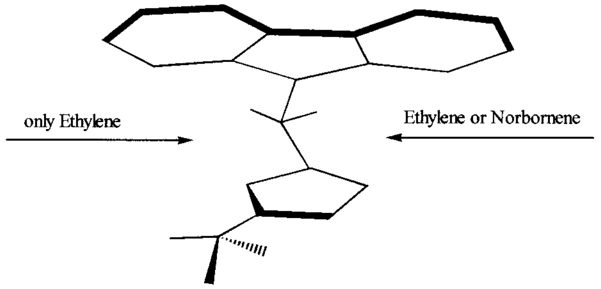
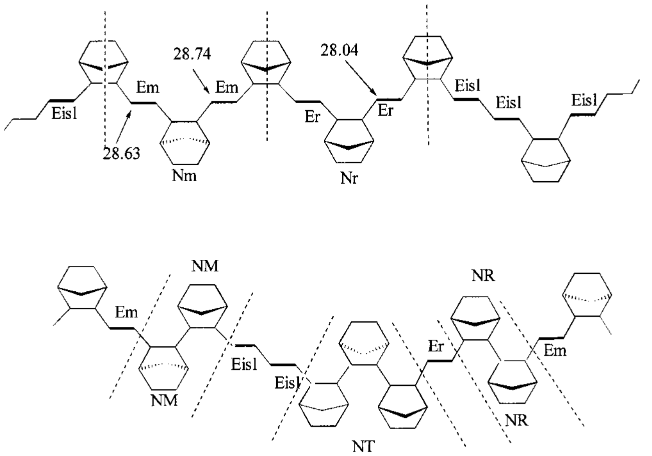


Figure 2. C_1 catalysts **1** [R = Me or Ph, R′ = Me or *tert*-butyl], **2a**, and **2b** for alternating ethylene–norbornene copolymerization: **1a** (R = Me, R′ = *tert*-butyl); **2a** (M = Zr); **2b** (M = Hf).

Scheme 1



Scheme 2



ing the observed peak areas of the assigned ^{13}C signals and accounting for the stoichiometric requirements.[13] Scheme 2 below illustrates the different types of sequences defined in the calculation, which also distinguishes between *meso* (*m*) and *racemic* (*r*) alternating units and between *meso* (*M*) and *racemic* (*R*) ENNE sequences.

The microstructure as well as the tacticity of the alternating copolymers will be described on the basis of the above procedure. Such a description evidences and quantifies differences in copolymer microstructures of the copolymers prepared with catalysts **3** and **4**, in particular their different *meso* and *racemic* NEN contents. The influence of the catalyst structure on the microstructure and on the tacticity of the copolymers will also be considered. Finally the relationship between the glass transition temperature (T_g) of the copolymers and their microstructure will be discussed.

Results and Discussion

Microstructure of the Copolymers Prepared with *rac*-Me_2Si(2-Me-[*e*]-benzindenyl)$_2ZrCl_2$. Copolymerizations of ethylene and norbornene were carried out with **3**/MAO, using a variety of conditions. The polymerization tests were not designed to investigate the catalytic activity of the catalytic system but rather to have low polymer 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 10–15%. 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 thermal analysis of selected copolymers are summarized in Table 1. The copolymers produced exhibit norbornene contents of 44.1–47.5 mol %. Average molecular weights of the copolymer are high (above 50 000), and molecular weight distributions are generally narrow.[14] In Figure 4, the ^{13}C NMR spectrum of an E–N copolymer synthesized with the C_2-symmetric bridged metallocene *rac*-Me_2Si(2-Me-[*e*]-benzindenyl)$_2ZrCl_2$ (**3**) shows five major signals, as expected for an alternating copolymer.[4a,7d,11] A complete description of sample KM101 can be found in the Supporting Information of ref 13.

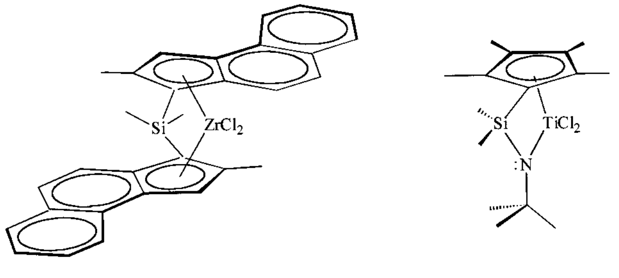
The signal assignments were checked by a ^{13}C–^{13}C correlated NMR spectrum using the INADEQUATE sequence, as already reported,[7d] and agree with those reported in the recent literature.[8b,10b] Figure 5 reports the typical values for chemical shifts of alternating copolymers prepared with catalyst **3**. The five major signals correspond to the perfectly alternating sequence (NENEN), while carbons of alternating units adjacent to different sequences (NENN, NENEE) give rise to slightly shifted signals.

Because of the C_2 symmetry of the metallocene used, the alternating NEN sequences present in this copolymer are highly isotactic, as indicated in the spectrum of Figure 4 by the predominance of the signals assigned in the left side of Figure 5. An alternating copolymer

Table 1. Copolymerization Data of E−N Copolymers Prepared with *Rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (3)[a]

sample	$P_{ethylene}$ (atm)	N/E [b]	N incorp (mol %)[c]	yield (g)	norbornene conversion (%)	M_n[d]	M_w/M_n[d]	T_g (°C)
KM103	0.17	26.6	44.1	0.042	1.1	68 334	1.51	114
KM102	0.25	26.3	45.2	0.084	1.6	n.d.	n.d.	115
KM105	0.20	21.7	46.7	0.363	8.6	173 943	4.14	117
KM97	1	26.3	47.0	0.139	0.7	51 296	1.17	122
KM104	1	23.2	47.5	1.150	5.5	72 507	1.97	122

[a] Polymerization conditions: [Zr] = 0.016 ÷0.032 mmol/L, Al/Zr = 2100, solvent = toluene 50 mL, T = 30 °C. [b] N/E = monomer feed ratio (mol/mol). [c] Norbornene incorporated in the copolymer by ^{13}C NMR. [d] GPC molecular weights and polydispersities vs polystyrene by viscometry.



3 **4**

Figure 3. Catalysts *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**) (C_2) and $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**) (C_1) for alternating ethylene−norbornene copolymerization.

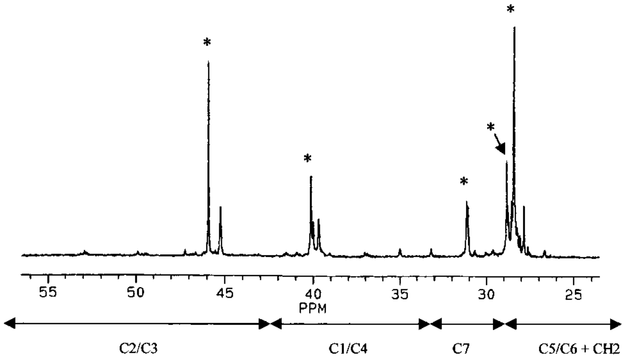


Figure 4. ^{13}C NMR spectrum of the ethylene−norbornene copolymer KM101 prepared with the *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**) and MAO catalyst at N/E feed ratio = 26.3 at 30 °C. The five major peaks of pure alternating isotactic sequence are marked with star.

would result from the impossibility of inserting a norbornene once a norbornene has already been inserted, even in the presence of a rather high norbornene concentration. Thus, the formation of NN diads is disfavored. On the contrary, the insertion of norbornene is more likely after an ethylene unit, so that NE diads are formed. However, a detailed inspection of the spectrum in Figure 4 reveals signals of isolated norbornene units (from EENEE sequences), as well as a great number of low-intensity signals due to norbornene microblocks, which are typical of E−N copolymers containing more than 50 mol % of norbornene and prepared, e.g., with a *rac*-$Et(indenyl)_2Cl_2$-based catalyst.[13] Indeed, when norbornene diads or triads are present, a greater number of signals is expected, as the signals of each carbon have different chemical shifts depending on the microstructural environment. In particular, signals at 26.24 (carbon C5) and at 47.12 ppm (carbon C3) are diagnostic for the presence of ENNE isotactic sequences.[7d,9] These features imply that instead of having only “pure” alternating sequences as represented in Figure 1, some NEN sequences are next to norbornene microblocks or longer ethylene sequences. The presence of norbornene in diads and in triads in sample KM101 is shown in Figure 6, which plots the percentages of N and E of different sequences computed with the above-mentioned procedure. The pattern of Figure 6 is characteristic of all the copolymers with norbornene content above 40 mol % prepared with catalyst **3**.[16] This is shown in Table 2 which reports the microstructure of the samples of Table 1.

Our procedure for analyzing the ^{13}C NMR spectra of these copolymers currently yields a complete description of the E−N chain at tetrad level, besides providing some information at higher level and distinguishing between *meso* and *racemic* alternating sequences and between *meso* and *racemic* NN diads. In Table 2, we choose to represent the chain composition by means of the molar percentages of norbornene in the different sequences; the percentages of alternating and isolated ethylene are added in order to complete the description at tetrad level. Inspection of Table 2 indicates that the pattern shown in Figure 6 for sample KM101 holds for all copolymers prepared with **3**: indeed, the data show that in these prevailingly alternating copolymers the mol % of norbornene in triads or longer norbornene homosequences is greater than the mol % of norbornene in diads. This surprising result is even more evident in copolymers with lower N content. Close inspection of Table 2 reveals that the microstructure of KM105 is not affected by the unusual M_w/M_n ratio of this copolymer sample, lying well between those of KM103 and KM104, which have lower and higher norbornene content, respectively, and narrow M_w/M_n.

Microstructure of the Copolymers Prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$. The half-sandwich $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**) precursor was known to yield prevailingly alternating E−N copolymers.[10a,12] Table 3 reports the selected copolymerization data concerning a series of copolymers prepared with catalyst **4** at growing N/E monomer feed ratios. The amount of incorporated norbornene grows as the N/E feed ratio increases up to a value of about 18/1, then reaches a plateau value of about 44 mol % in agreement with previous findings.[12] With the help of conformational analysis,[7e] we have predicted stereochemical shifts in alternating copolymers and evidenced the presence of *racemic* as well as *meso* alternating sequences (see Figure 1) in the copolymers prepared with this precursor.[13]

Figure 7B shows the spectrum of a copolymer prepared with **4** presenting alternating *meso* and *racemic* NEN sequences. In Figure 7A, the spectrum of an isotactic alternating copolymer synthesized with *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**3**), with similar norbornene content, is reported for comparison.

The signals of the carbon atoms of a *racemic* alternating NEN sequence are characterized by an upfield shift

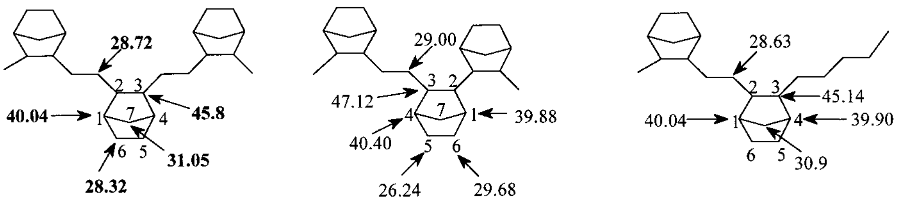


Figure 5. Chemical shifts (ppm) of mainly *meso* alternating E−N copolymers. For brevity only chemical shifts of E alternating carbons and of the central N unit are listed; major signals in bold characters. Chemical shifts are referenced to HMDS. The spectra were measured in $C_2D_2Cl_4$ at 105 °C. Carbon numbering according to ref 11.

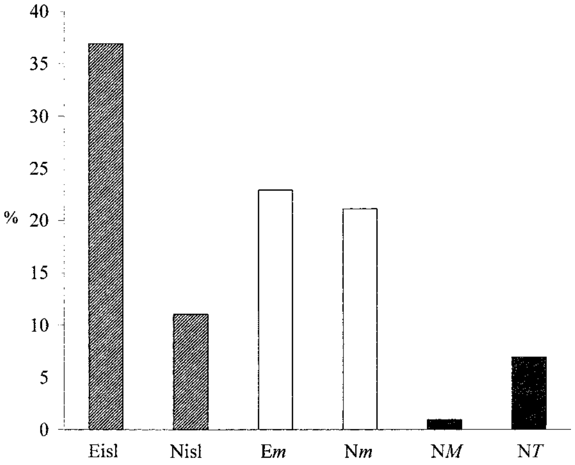


Figure 6. Percentages of norbornene and ethylene in different sequence types, defined as reported in ref 13, and calculated for sample KM101 of Figure 4. Key (See Scheme 2): Eisl, f_E(isl); Nisl, f_N(isl); E*m*, *f*(*m*); N*m*, f_N(*m*); N*M*, f_N(*M*); N*T*, f_N(triad) or f_N(block).

with respect to those of a *meso* alternating sequence (belonging to an isotactic copolymer). Indeed, the secondary ethylene carbon atoms belonging to a *racemic* alternating sequence are evidenced at 28.04 ppm, while the isotactic analogue appears at 28.73 ppm. Similarly, when looking at the region of the bridgehead carbon atoms C1/C4, a new peak, which appears at 39.54 ppm, is assigned to a *racemic* alternating sequence, whereas the peak of the isotactic alternating sequence was assigned at 39.9 (NENEE) and 40.04 (NENEN) ppm. Finally, the C2/C3 signal of the *racemic* sequence appears at 45.21 ppm whereas the *meso* sequence appears at 45.73 and 45.82 ppm. The bridged carbon atom region is not sufficiently resolved to evidence any difference. It is worth noting that while the C1/C4 and C2/C3 *racemic* alternating signals often overlap with the corresponding isolated signals, the ethylene peak at 28.04 ppm is the true diagnostic signal characterizing the presence of the *racemic* alternating sequence at first glance of a spectrum of E−N copolymers with N content around 40 mol %.

It is worth recalling that catalyst **4**, as already known,[10a,12] shows a very high propensity to yield alternating copolymers and produces a very small amount of norbornene microblocks.

Mechanism of Polymerization: Relationships between the Nature of the Catalyst and the Microstructure of the Polymers Obtained. Quantitative differences between the microstructures of two copolymers having roughly the same norbornene content incorporated but prepared with the two different catalysts are evident in the graphs of Figure 8, where the total ethylene and norbornene amounts have been broken into molar fractions of the most interesting sequences. Indeed, *rac*-Me_2Si(2-Me-[*e*]-benzindenyl)$_2$$ZrCl_2$ yields an isotactic alternating copolymer which is much blockier than the alternating copolymer containing *meso* and *racemic* NEN sequences obtained with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$.

As both copolymers were synthesized under analogous conditions (i.e., same reaction temperature, similar norbornene and ethylene concentrations, and comparable Al/Zr ratios), the tacticity of the alternating sequence and the propensity to alternate the comonomers depend only on the structure of the catalyst employed and on the differences in the polymerization mechanism.

It has been proposed that the formation of alternating ethylene norbornene copolymers with C_1 catalysts occurs through a chain migratory mechanism, as shown in Scheme 1.[10a] The growing polymer chain migrates to the site where initially the olefin is coordinated. Consequently, each insertion alternately occurs at one or at the other of two metallocene coordination sites. When a C_1 catalyst such as *i*-Pr[(3-*t*-Bu-Cp)Flu]$ZrCl_2$ (**1a**) is used, the *tert*-butyl group and half of the fluorenyl ligand hinder the coordination of the norbornene on one site, and only ethylene, the less bulky of the two olefins, can be inserted. Since both olefins can be inserted at the less hindered side, a copolymer with an alternating structure can be formed by this group of catalysts in the presence of great eccess of norbornene. Group 4 bridged monocyclopentadienyl catalysts such as μ-Me_2-Si(3-*tert*-butylcyclopentadienyl)(adamantylamido)Me_2 [M = Zr, **2a** or Hf, **2b**] would yield alternating ethylene−norbornene copolymers through a similar mechanism.[11] Similarities in the catalyst structures are observable in Figure 2. Therefore, an alternating ethylene−norbornene copolymer would result from the use of a catalyst with two heterotopic sites.

The C_2-symmetric bridged metallocene *rac*-Me_2Si(2-Me-[*e*]-benzindenyl)$_2$$ZrCl_2$ (**3**) used in the present work is a catalyst with two homotopic sites (Figure 3), and in principle, both monomers should have the same probability of being inserted at both sides. Indeed, other C_2-symmetric bridged metallocenes such as *rac*-Me_2Si-(indenyl)$_2$$ZrCl_2$ (**5**) give rise to more random copolymers under the same conditions.[7f] Thus, the alternating structure of this copolymer would seem rather surprising at first. However, with respect to **5**, **3** has substitutions in indenyl positions 2, 4, and 5, which permit this catalyst to produce highly isotactic polypropylene, with high molecular weights and high yields.[18] The steric hindrance of the ligand structure seems to forbid two consecutive norbornene insertions at the two homotopic sites, so that a mainly alternating copolymerization occurs with this catalyst, with or without chain migratory insertions (Scheme 3, where the sketched interactions are only indicative, not modeled by calculations).

Table 2. Microstructure of E−N Copolymers Prepared with *rac*-Me_2Si(2-Me-[*e*]-benzindenyl)$_2ZrCl_2$ (3)

sample	molar percentages[a]										
	N	Nisl	N*m*	N*r*	N*M*	N*R*	N*T*	Eisl	E*m*	E*r*	N*T*/N*M*
KM101	40.2	11.0	21.1	0.0	0.9	0.0	6.9	36.9	22.9	0.0	7.6
KM103	44.1	9.0	25.2	0.0	0.8	0.0	9.0	28.2	27.7	0.0	11.2
KM102	45.2	8.6	25.4	0.0	2.4	0.0	8.8	26.4	28.4	0.0	3.7
KM105	46.7	8.6	26.0	0.0	2.5	0.0	9.5	24.0	29.3	0.0	3.8
KM106	47.4	8.0	28.7	0.0	3.0	0.0	7.7	20.7	31.8	0.0	2.6
KM104	47.5	6.6	28.9	0.0	4.2	0.0	7.8	19.7	32.7	0.0	1.9

[a] Defined and computed according to the procedure described in ref 13. Key (see Scheme 2): Eisl, f_E(isl); Nisl, f_N(isl); E*m*, *f*(*m*); E*r*, *f*(*r*); N*m*, f_N(*m*); N*r*, f_N(*r*); N*M*, f_N(*M*); N*T*, f_N(triad) or f_N(block).

Table 3. Copolymerization Data of E−N Copolymers Prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (4)[a]

sample	N/E [b]	N incorp (mol %)[c]	yield (g)	norbornene conversion (%)	M_n [d]	M_w/M_n[d]	T_g (°C)
KM77	15.5	35.1	0.137	1.0	73 989	1.93	98
KM74	18.3	40.1	1.640	11.3	66 111	1.88	107
KM107	28.1	42.1	0.482	2.1	229 854	3.39	112
KM108	21.7	43.6	0.931	5.5	71 624	4.73	109

[a] Polymerization conditions: [Ti] = 0.016÷0.032 mmol/L, Al/Zr = 2100, solvent = toluene = 50 mL, T = 30 °C, $P_{ethylene}$ = 1 atm [b] N/E = monomer feed ratio (mol/mol). [c] Norbornene incorporated in the copolymer by ^{13}C NMR. [d] GPC molecular weights and polydispersities vs polystyrene by viscometry.

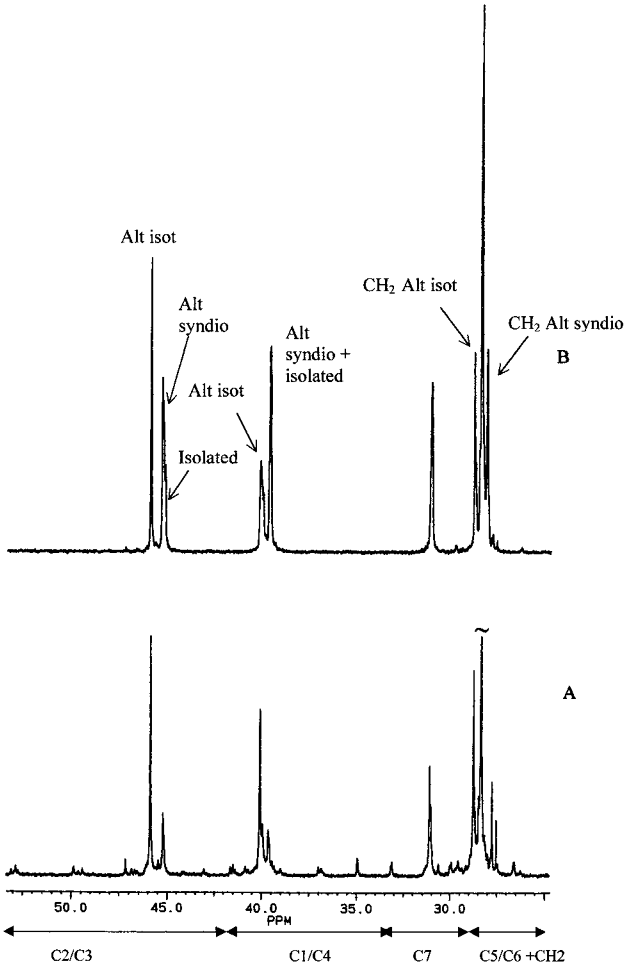


Figure 7. ^{13}C NMR spectra of copolymer samples KM103 (A) prepared with *rac*-Me_2Si(2-Me-Benz-[e]-Indenyl)$_2ZrCl_2$ (**3**) and KM108 (B) prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (**4**).

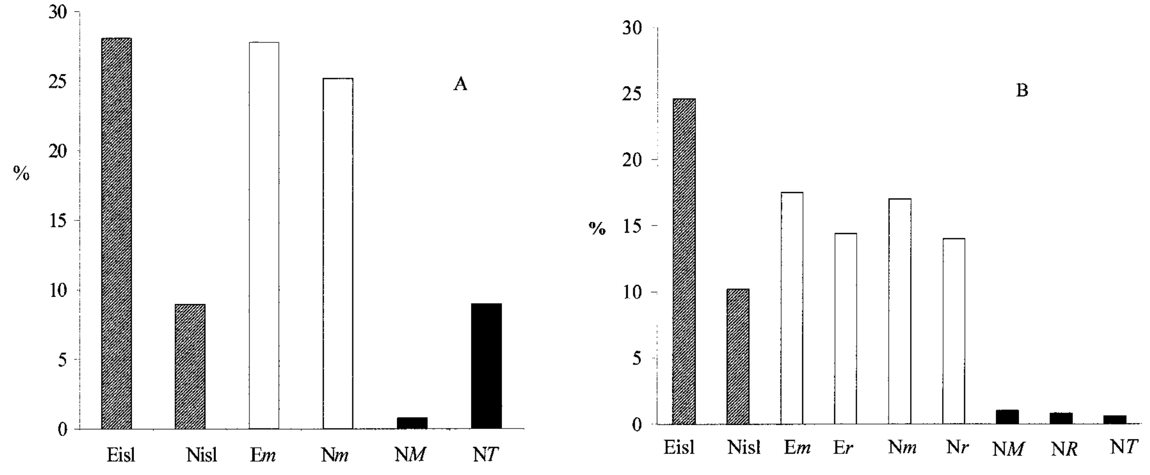
However, as soon as two successive norbornene units are added—probably to avoid strong nonbonded interactions between the hindered growing polymer chain and the indenyl substituents—some changes in the interactions occur which favor the insertion of a third norbornene unit. Strong nonbonded interactions due to steric hindrance have been invoked as the cause of the formation of *rrrr* errors in isotactic polypropylene with Me_2C(Flu)(3-*tert*-butyl-Cp)$ZrCl_2$-based catalysts.[21]

When the structures of the two catalysts **3** and **4** are compared, it seems reasonable that the permethylation of the Cp ligand increases the steric crowding at the upper half of **4,** which could push the growing polymer chain toward the lower half, that is, toward the same half which should favor the norbornene approach (Scheme 3). From this perspective, addition of a second norbornene unit should be much more hindered with respect to the insertion of an ethylene unit, after a first insertion of norbornene, and the insertion of a third norbornene would be almost impossible. This could thus explain why the half-sandwich catalyst produces a much more alternating copolymer. The presence of both *meso* and *racemic* NEN sequences and *meso* and *racemic* NN diads could be explained by similar probabilities for norbornene to coordinate and insert at the left or the right coordination sites.

Relationship between Thermal Properties and Microstructure. One of the main interests in E−N copolymers derives from their high glass transition temperatures. The results of thermal analysis of the copolymers prepared with catalyst **3** and **4**, which all have high molecular weights, were reported in Tables 1 and 3, respectively.

The glass transition temperatures of copolymer samples obtained with **3** with percentages of N in the range 44−47.5% were found to be between 114 and 122 °C; the DSC profiles did not show any evidence of melting endotherms. These T_g values are rather close to those found for perfectly alternating ethylene−norbornene copolymers (T_g above 110 °C),[11] which are semicrystalline materials with melt temperatures between 235 and 285 °C. Thus, our results indicate that the interruption of the alternating structure regularity due to the presence of EENEE and ENNE sequences prevents crystallization.

To examine the relationship between the T_g of a copolymer and its norbornene content, T_g values for the samples of Tables 2 and 4 have been plotted against the norbornene content (Figure 9). As expected, T_g increases with the norbornene percentage, but, from these data, a poor correlation between the two param-

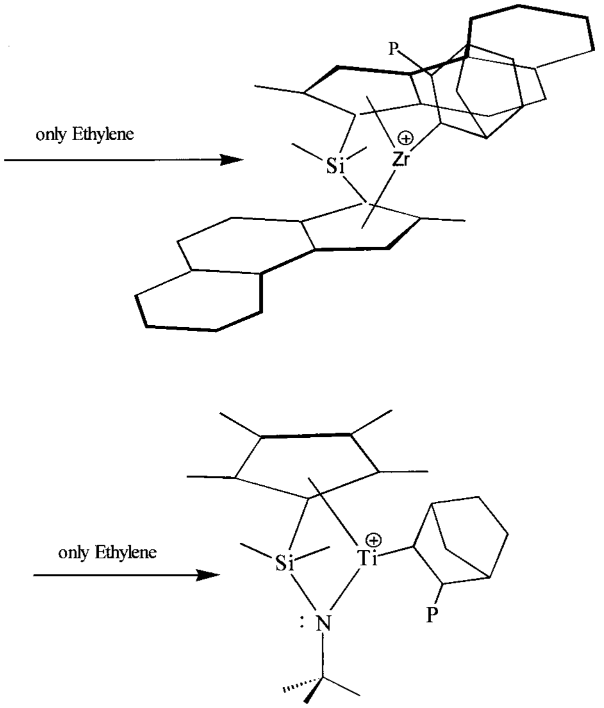


rac-Me$_2$Si(2-Me-[e]-benzyndenil)$_2$ZrCl$_2$ **(3)** Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ **(4)**

KM 103 N = 44.1 % *KM 108* N = 43.6 %

Figure 8. Percentages of norbornene and ethylene in different sequence types, defined as reported in ref 13, and calculated for samples KM103 and KM108 of Figure 7, parts A and B, respectively. Key (see Scheme 2): Eisl, f_E(isl); Nisl, f_N(isl); E*m*, f(*m*); N*m*, $F_N(m)$; N*M*, $f_N(M)$; N*T*, f_N(triad) or f_N(block).

Scheme 3



eters is found. In our opinion, the T_g differences should not arise from differences in M_n since all the copolymers have rather high M_n values (>50 000).

The relationship between T_g and microstructures will be further discussed in a following paper on the basis of the analysis of a great number of copolymers whose complete ^{13}C NMR analysis is reported in ref 13.

We only anticipate that results of such an analysis indicate that indeed the behavior of T_g vs the copolymer composition is much better described by a linear equation including the molar fractions of *m* and *r* sequences, besides the total norbornene content, with different T_g contributions for the two types of alternating sequences. This effect could arise from differences in the most stable conformations of *meso* and *racemic* alternating sequences.

Conclusions

In summary, we report the synthesis and analysis of E−N copolymers obtained with the C_2 metallocene **3** and with the C_s constrained geometry catalyst **4**. The former catalyst yields stereoregular alternating copolymers while in the second case stereoirregular alternating copolymers are found. ^{13}C NMR analysis and quantitative computation of polymer sequence distribution and tacticity evidenced and quantified the major differences between the polymers. The mainly alternating copolymer prepared with **4** contains both *meso* and *racemic* NEN sequences and a small amount of *meso* and *racemic* NN diads. The alternating copolymer prepared with **3** contains only *meso* NEN sequences. The formation of NN diads is disfavored with both catalysts. Surprisingly, a significant amount of NNN triads (T) is obtained with the C_2 catalyst. Differences in catalyst symmetry and ligands suggest the origin of the differences in the tacticity of the alternating sequences. The bulkiness of the catalyst ligands, of the growing polymer chain and of the norbornene could cause strong nonbonded interactions which explain the limited formation of norbornene diads under these conditions. It is more difficult to guess the nature of the interactions which after two successive norbornene insertions with the bulky catalyst **3** favor the insertion of a third norbornene unit. The presence of NNN triads in a mainly alternating copolymer seems to indicate that various mechanisms are at work for the C_2 symmetric catalysts. Penultimate effects (second-order Markov statistic) might play a decisive role in these copolymerizations as already suggested in E−N copolymerizations obtained with different metallocene catalysts.[8a,10b] The surprising structure of the alternating E−N copolymer obtained with **3** confirms the great potential of metallocene catalysts in tailoring polymer structure. Our current level of calculations of molar fractions of E−N copolymers at tetrad level can be translated into the conventional description in terms of tetrads or pentads. This will help one to clarify the statistics of these copolymerizations and to test the possible copolymerization mechanisms.

Table 4. Microstructure of E−N Copolymers Prepared with $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (4)

sample	molar percentages[a]										
	N	Nisl	N*m*	N*r*	N*M*	N*R*	N*T*	Eisl	E*m*	E*r*	N*T*/N*M*
KM77	35.1	14.6	12.2	6.9	0.0	1.4	0.0	45.5	12.4	7.0	0.0
KM74	40.1	14.9	16.0	9.2	0.0	0.0	0.0	34.7	16.0	9.2	0.0
KM107	42.1	10.0	19.1	10.1	0.7	1.4	0.8	27.5	19.8	10.6	1.1
KM108	43.6	10.2	17.0	14.0	0.9	0.9	0.6	24.5	17.5	14.4	0.7

[a] Defined and computed according to the procedure described in ref 13. Key (see Scheme 2): Eisl, f_E(isl); Nisl: f_N(isl); E*m*, f(*m*); E*r*, f(*r*); N*m*, $f_N(m)$; N*r*, $f_N(r)$; N*M*, $f_N(M)$; N*T*, f_N(triad) or f_N(block).

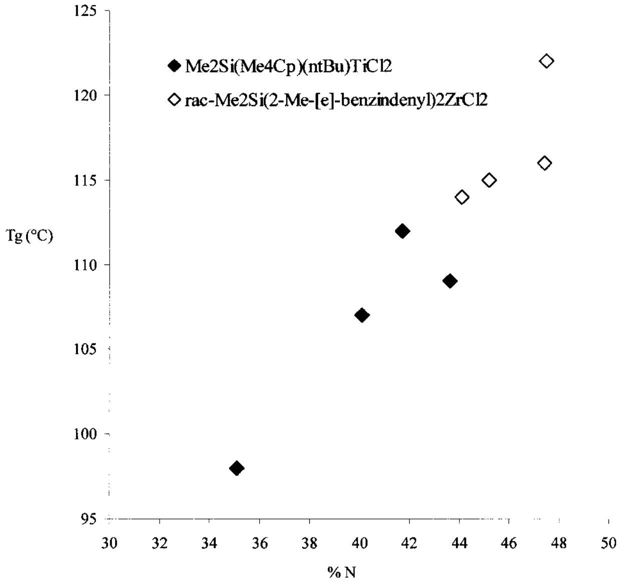


Figure 9. Glass transition temperatures vs norbornene content of E−N copolymers of Tables 1 and 3.

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. $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ was purchased from Boulder. *rac*-Me_2Si(2-Me-[*e*]-benzindenyl)$_2ZrCl_2$ was synthesized as part of the TMR network in the group of Prof. Brintzinger. Ethylene was dried on $CaCl_2$ and molecular sieves. Oxygen was removed by fluxing the gas through BTS catalysts. Norbornene was distilled from sodium.

Polymer Synthesis. In a typical experiment, ethylene−norbornene copolymerizations were performed at 30 °C in a 250 mL round-bottomed Schlenk flask. After 3 vacuum−nitrogen cycles, norbornene was introduced into the reactor. Toluene (50 mL) was then cannula transferred, and the methylaluminoxane (MAO) was added as a toluene solution ($[Al] = 1.74\ \text{mol}\cdot\text{L}^{-1}$). 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 $[Zr] = 0.016\ \text{mmol}\cdot\text{L}^{-1}$, Al/Zr = 2100). Copolymerization reactions were stopped before the medium would become heterogeneous and before 10−15% of the initially introduced norbornene was consumed. The maximum reaction time was 3 h. 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 (50 °C). In the polymerization experiments with ethylene partial pressure lower than 1 atm, after degassing, nitrogen was added to bring the pressure to a known value. Total pressure was subsequently brought to atmospheric pressure with ethylene.

Ethylene concentration in toluene was calculated according to Henry's law

$$C_{\text{Ethylene}} = P_{\text{Ethylene}} \times H_o \exp\left(\frac{\Delta H_L}{RT}\right)$$

where C_{Ethylene} = ethylene concentration (mol L^{-1}); P_{Ethylene} = ethylene pressure (atm); H_o = Henry coefficient = 0.00175 $\text{mol}\cdot\text{L}^{-1}\cdot\text{atm}^{-1}$; ΔH_L = enthalpy of solvatation of ethylene in toluene = 2569 $\text{cal}\cdot\text{mol}^{-1}$; $R = 1.989\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Characterization. ^{13}C NMR. 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 established previously:

$$\text{Mol N \%} = \frac{\frac{1}{3}[2I_{C_7} + I_{C_1-C_4} + I_{C_2-C_3}]}{I_{CH_2}} \times 100$$

where I_{CH_2}, I_{C_7}, $I_{C_1-C_4}$, and $I_{C_2-C_3}$ are the total peak areas in the ranges 26−30, 30−36, 34−42, and 43−54 ppm.

DSC Measurements. Measurements were done on a Pyris 1 Perkin-Elmer instrument. The samples (around 5 mg) were heated from 50 to 250 °C at 20 °C/min, with a nitrogen flow (30 mL/min). A first scan was realized to erase the thermal history of each polymer. T_g were then recorded during a second thermal cycle.

Molecular Weight Measurements. GPC measurements were performed in *o*-dichlorobenzene at 105 °C by a GPCV2000 size exclusion chromatography (SEC) system from Waters equipped with two online detectors: a viscometer and a differential refractometer. The column set was composed of three mixed TSK-Gel GMH_{XL}-XT columns from Tosohaas. The system was calibrated using polystyrene standards.

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Supporting Information Available: Text giving definitions of the molar fractions of stereosequences of E-N copolymers (including a structural diagram) used to describe and to quantitatively determine the copolymer microstructure according to a method reported in ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Some E−N copolymer samples show molecular weight distributions which are unusual for single site metallocene catalysis. It has been already reported that determination of molecular weights of E−N copolymers is complicated by low d*n*/d*c*.[12, 15] The results reported here were obtained by viscometry, while refractive index detection gave narrower molecular weight distribution for all the samples. We cannot exclude that the anomaly of some samples is due to the unusual viscosities of copolymers very rich in norbornene.

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(16) In Figure 5, assignments of carbons C2/C3 of NN account for the correction of an error that occurred in ref 13, originating from nomenclature misunderstandings.

(17) We exclude that the presence of NNN microblocks, the characteristic feature of E−N copolymers prepared with catalyst **3,** arises from fractions of norbornene homopolymers, as suspected by a reviewer. We have obtained only 200 mg of homopolymers at 70 °C in 4 days with catalyst **3** under [Zr] and Zr/Al molar ratios similar to E−N copolymerizations. Hence, the homopolymerization appears practically impossible in copolymerizations that are performed at 30 °C for a maximum reaction time of 3 h.

(18) It is also reported that addition of a 4,5-annealated aromatic ring in **3** yields an increased tolerance of this catalyst, with respect to **5**, toward the steric hindrance of the olefin, as shown by the capability of this complex to induce a polymerization of branched olefins such as 3-Me-1-pentene.[19,20]

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