Macromolecules

Volume 32, Number 22 November 2, 1999

Microstructure of Ethene/Norbornene Copolymers[†]

Michael Arndt-Rosenau* and Inken Beulich

Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

Received November 23, 1998

ABSTRACT: The microstructure of ethene/norbornene copolymers produced by metallocene/methylaluminoxane catalysts is investigated by ^{13}C NMR spectroscopy. The microstructure of alternating copolymers is assigned on the pentad level by comparison of the pentad distribution in ^{13}C NMR spectra with the calculated distribution according to the alternating mechanism. Norbornene block structures produced with different catalysts are compared, and norbornene diblock structures are assigned. Triad distributions for the alternating copolymers and diad distributions for copolymers containing diblocks were obtained.

Introduction

Polymerization of cycloolefins with homogeneous metallocene catalysts occurs by vinyl polymerization.[1−7] Polynorbornenes feature two chiral centers per norbornene unit and are therefore ditactic. It is widely accepted that norbornene inserts into Zr−H and Zr−C bonds via a 2,3 cis−exo orientation in homo- and copolymerizations.[8] Cis−exo insertion results in erythroditactic polymers. Hydrooligomerizations of norbornene have been used to produce hydrodimers and trimers. Their microstructure has been assigned and correlated to the symmetry of the metallocenes. Assuming the same mechanism as in the polymerization of α-olefins, the stereogenic C_s symmetric metallocenes produce erythrodisyndiotactic polymers whereas C_2 symmetric metallocenes are expected to form erythrodiisotactic products.[9] A single inversion of relative topicity causes a racemic (meso) linkage in the product of C_s (C_2) symmetric catalysts.

Copolymers of norbornene and ethene possess rather interesting material properties such as high glass transition temperatures in combination with a good chemical resistance and excellent transparency. Because of their rigid cyclic monomer units, they show a high refractive index and are therefore suitable for optical applications.[10] Although they have been known for several years now, there have been only a few studies on their microstructure.[11−19]

While it is straightforward to calculate the norbornene content X_N in the copolymers from the four peak groups in the ^{13}C NMR spectrum (see A−D in Figure 1, Figure 2, Table 1 and eq 1), the ^{13}C NMR spectra are otherwise very complex. Apart from different comonomer sequences, norbornene blocks of varying lengths and the stereochemistry of norbornene, norbornene linkages cause extensive signal splitting.

$$X_N = \frac{\frac{1}{5}[I(\mathrm{C2,C3}) + I(\mathrm{C1,C4}) + I(\mathrm{C7})]}{\frac{1}{2}[I(\mathrm{C5,C6}) + I(\mathrm{C}\alpha,\mathrm{C}\beta,\mathrm{C}\gamma,\mathrm{C}\delta)]} = \frac{2}{5}\,\frac{5N}{2N + 2E} = \frac{I(\mathrm{A}) + I(B) + I(C)}{2.5I(D)} \quad (1)$$

Signals of ethene sequences appear between 33 and 28 ppm and overlap with resonances of C5 and C6 of the cyclic unit. No increment systems are available for calculating resonances of cyclic units. Signal groups overlap if the norbornene content rises to over 60 mol %, no separate peaks can be distinguished, and longer norbornene sequences give rise to many signals, which are the source of the difficulties with the assignments of the very complex ^{13}C NMR spectra of homopolynorbornene.

Several groups have tried to assign the ^{13}C NMR spectra of ethene/norbornene copolymers containing isolated and alternating norbornene units,[11−16] but none of them were able to assign the peaks between 28 and 33 ppm in detail, so it was not even possible to calculate triad distributions for copolymers containing no blocks of norbornene.[28]

More recently, Bergström et al. utilized 2D NMR techniques to investigate ethene/norbornene copolymers

---

[†] Dedicated to Prof. G. Fink on occasion of his 60th birthday.

* Corresponding author. E-mail arndt@chemie.uni-hamburg.de.

10.1021/ma981813z CCC: $18.00

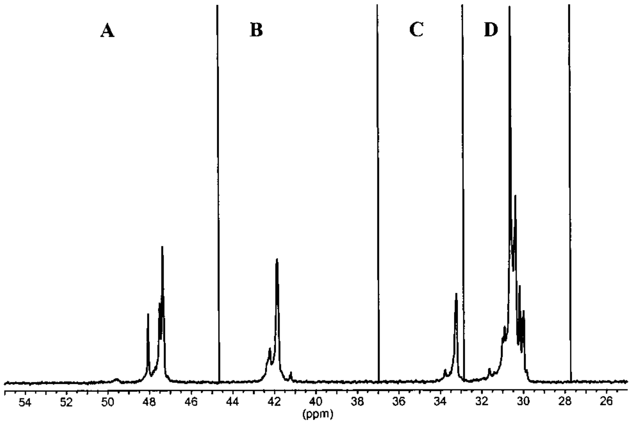


Figure 1. ^{13}C NMR spectrum of an ethene/norbornene copolymer measured in perchlorobutadiene/1,1,2,2-tetrachlorodideuterioethane (10/1) at 100 °C and definition of the regions A to D.

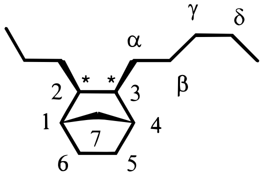


Figure 2. Denomination of carbon atoms of an ethene/norbornene copolymer used in this paper.

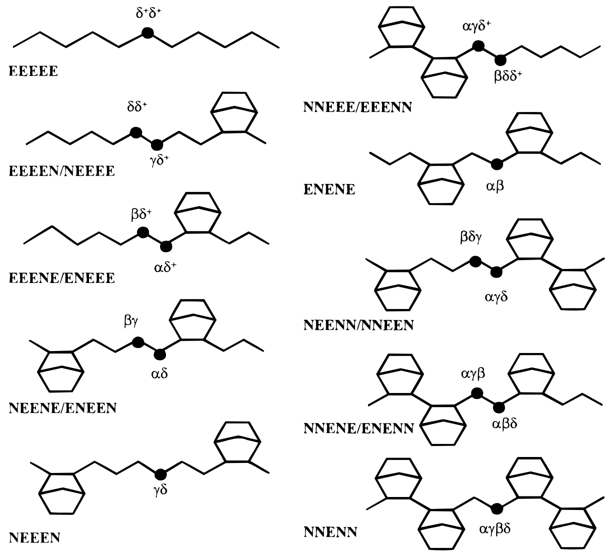
Table 1. ^{13}C NMR Assignments of Ethene/Norbornene Copolymers into Four Separate Peak Groups[a]

^{13}C chemical shifts [ppm]	assignments	peak group
56−45	C2, C3	A
45−37	C1, C4	B
37−33	C7	C
33−28	C5, C6, Cα, Cβ, Cγ, Cδ	D

[a] Proton broad band decoupled ^{13}C NMR spectra were measured in hexachlorobutadiene/1,1,2,2-tetrachloro-1,2-dideuterioethane (3 mL/0.3 mL in 10 mm tube) at 100 °C on a Bruker-MSL-300 spectrometer. All chemical shifts were referenced to the solvent shift of d_2-TCE at 74.24 ppm.

produced by *rac*-[Et(Ind)$_2$]ZrCl$_2$/MAO.[18] They were able to attribute resonances of norbornene diads and also identify some resonances caused by longer blocks of norbornene.[29] Tritto et al. used an approach very similar to the one described below by comparing the spectra of copolymers with different compositions and produced by different catalysts, to assign the resonances.[19] They did not assign resonances between 35 and 43 ppm, and our investigations, which are based on many more samples, show some of their assignments to be doubtful.[30] Nevertheless their investigations, as well as results obtained in our group, showed that splitting occurs at least to some of the signals on a pentad level.

Chart 1. Denomination of Norbornene-Centered Pentads and Carbon Atoms in Ethene/Norbornene Copolymers



If we neglect effects of stereochemistry, we deal with a simple copolymer, and therefore we can expect 20 magnetically inequivalent pentads. Ten of these are ethene and 10 are norbornene centered, six of each are unsymmetric, and four are symmetric (see Chart 1 and Chart 2). For symmetric pentads with a central ethene unit we should observe one resonance each, while those with a central norbornene unit will give rise to four signals in a 2:2:1:2 intensity ratio. Unsymmetric pentads with a central ethene unit feature two resonances, and for those with a norbornene central unit all seven carbon atoms are anisochronic. So in the case of all pentads being formed we may observe 4 × 1 + 6 × 2 (ethene) + 4 × 4 + 6 × 7 (norbornene) = 74 resonances.

As a convention for denominations C2 is always closer to another norbornene unit than C3; for example see C2(EENEN/NENEE) and C3(EENEN/NENEE) in Chart 2. C1, C4, and C5, C6 are named in the same way.

The triad distribution can be calculated according to the following equations:[31]

$$\mathrm{EEE} = I(\mathrm{C}_{\gamma\delta}) + I(\mathrm{C}_{\gamma\delta+}) + I(\mathrm{C}_{\delta\delta+}) + I(\mathrm{C}_{\delta+\delta+}) \quad (2)$$

$$\mathrm{EEN/NEE} = I(\mathrm{C}_{\alpha\delta+}) + I(\mathrm{C}_{\alpha\gamma\delta+}) + I(\mathrm{C}_{\alpha\delta}) + I(\mathrm{C}_{\alpha\gamma\delta}) + I(\mathrm{C}_{\beta\delta+}) + I(\mathrm{C}_{\beta\delta\delta+}) + I(\mathrm{C}_{\beta}\gamma) + I(\mathrm{C}_{\beta\delta\gamma}) \quad (3)$$

$$\mathrm{NEN} = I(\mathrm{C}_{\alpha\beta}) + I(\mathrm{C}_{\alpha\beta\delta}) + I(\mathrm{C}_{\alpha\gamma\beta}) + I(\mathrm{C}_{\alpha\gamma\beta\delta}) \quad (4)$$

$$\mathrm{ENE} = I(\mathrm{C2,C3(EENEE)} + I(\mathrm{C2,C3(EENEN/NENEE)} + I(\mathrm{C2,C3(NENEN)}) \quad (5)$$

$$\mathrm{NNE/ENN} = I(\mathrm{C2,C3(ENNEE/EENNE)} + I(\mathrm{C2,C3(NNNEE/EENNN)} + I(\mathrm{C2,C3(NNNEN/NENNN)} + I(\mathrm{C2,C3(ENNEN/NENNE)} \quad (6)$$

$$\mathrm{NNN} = I(\mathrm{C2,C3(ENNNE)}) + I(\mathrm{C2,C3(NNNNE/ENNNN)} + I(\mathrm{C2,C3(NNNNN)}) \quad (7)$$

Comparison of the resonances in the ^{13}C NMR spectra of copolymers with different compositions produced with different catalysts allows comonomer sequence assignments. Figure 3 gives a survey of the metallocenes used in this study.

Assignments of Alternating Ethene/Norbornene Copolymers. The [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO catalyst system produces only isolated and alternating sequences of norbornene in the copolymerization of ethene and norbornene at a polymerization temperature of 30 °C.[11,13,14,20] In a previous study we have shown that polymerization at 30 °C proceeds via an alternating mechanism.[11,13,14] No norbornene blocks and no even-numbered ethene blocks (NEENE/ENEEN) are observed; the ^{13}C NMR spectra are comparatively simple due to the fact that only eight pentads are possible. Figures 4 and 5 show the development of the spectra is

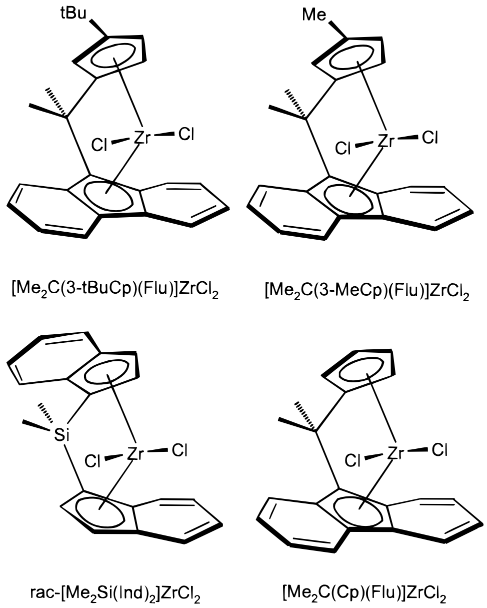
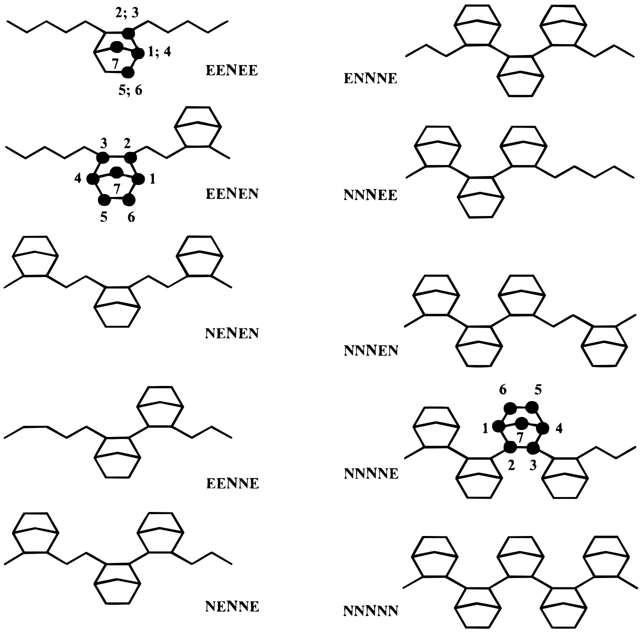


Figure 3. Structures of the metallocenes used for ethene/norbornene copolymerization.

Chart 2. Denomination of Ethene-Centered Pentads and Carbons Atoms in Ethene/Norbornene Copolymers



dependent on the incorporation rate of norbornene and the denomination of the resonances in the region A, B, C, and D.

The copolymers are highly erythrodiisotactic, and therefor no splittings of the resonances due to stereochemical effects are observed. A copolymerization model has been developed and applied to this catalysts system, and copolymerization parameters have been determined on the basis of the copolymerization equation which correlates the feed composition with the polymer composition.[14]

The pentad distribution can be calculated using copolymerization parameters obtained from the copolymerization equation: $r_E{}^A = 3.1$, $r_E{}^B = \infty$,[32] $r_N{}^A = 0$, and $r_N{}^B = 0$. Figure 6 compares the observed integrals for the resonances of region A to those calculated from the pentad distibution. The comparison shows that the resonances of C2 and C3 are tetrad-sensitive. Two resonances are observed for the stereoregular polymer. The signal at 48.05 ppm (A2) corresponds to the resonances for C2, C3 of the NENEN pentad overlapping with those of C3 of the EENEN/NENEE pentad. The signal at 47.35 ppm (A1) is assigned to the resonance of C2, C3 of the EENEE pentad overlapping with C2 of the EENEN/NENEE pentad; in contrast, Tritto et al. assigned the peak at 48 ppm for the sum of C2, C3(EENEN/NENEE) and C2, C3(NENEN).[19]

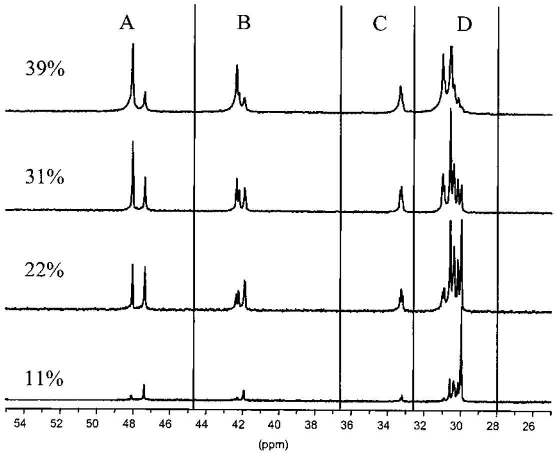


Figure 4. Copolymerization of ethene and norbornene by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO at 30 °C in toluene. ^{13}C NMR spectra of copolymers containing 11, 22, 31, and 39 mol % of norbornene.

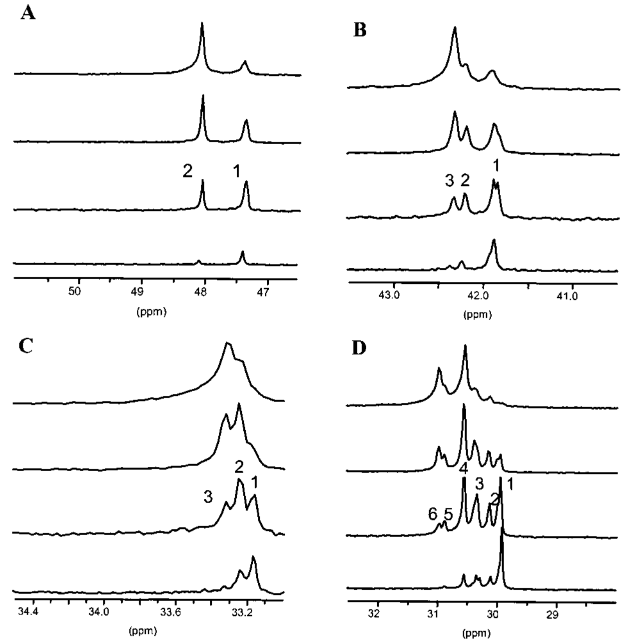


Figure 5. Copolymerization of ethene and norbornene by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO at 30 °C in toluene. Regions A to D of copolymers containing 11, 22, 31, and 39 mol % of norbornene; denomination of the peaks.

As can be seen in Figure 7 for region B the bridgehead carbon atom C1 is pentad-sensitive, distinguishing alternating (NENEN), isolated (EENEE), and intermediate (EENEN/NENEE) sequences while the resonances of C4 in isolated and intermediate structures overlap.

C7 gives rise to three different signals in region C, but the resolution of the spectra is not good enough for deconvolution-based correlation of experimental and

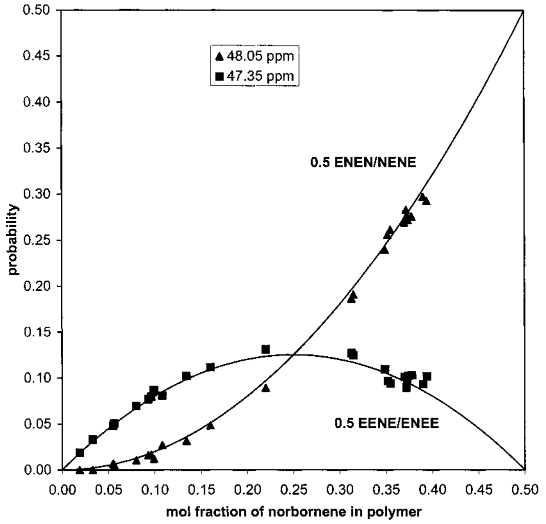


Figure 6. Copolymerization of ethene and norbornene by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO at 30 °C in toluene. Comparison of experimental peak intensity in the ^{13}C NMR spectra (▲, intensity of resonance at 48.05 ppm; ■, intensity of resonance at 47.35 ppm) with those calculated from the pentad distributions (lines). The pentad distribution is calculated by using copolymerization parameters determined from the copolymerization equation.

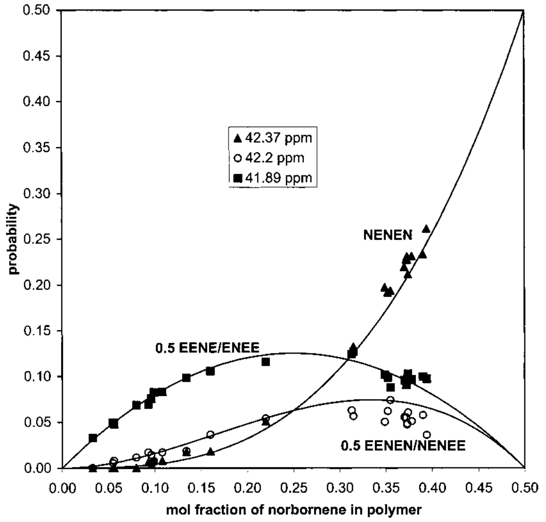


Figure 7. Copolymerization of ethene and norbornene by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO at 30 °C in toluene. Comparison of experimental peak intensity in the ^{13}C NMR spectra (▲, intensity of resonance at 42.37 ppm; ○, intensity of resonance at 42.2 ppm; ■, intensity of resonance at 41.89 ppm) with those calculated from the pentad distributions (lines). The pentad distribution is calculated by using copolymerization parameters determined from the copolymerization equation.

calculated integrals. Nevertheless, on the basis of their development with increasing norbornene, an assignment is possible. Figures 8 and 9 show the correlation of experimental and calculated integral for region D.

The resonances of C5 and C6 of the norbornene units give only one signal which is observed at 30.5 ppm. Tritto et al. proposed a spliting for resonances of C5 and C6 into signals at 30.9, 30.8, and 30.5 ppm. Our investigations showed that the sum of the intensities of these signals is higher than the norbornene content, indicating an incorrect assignment.

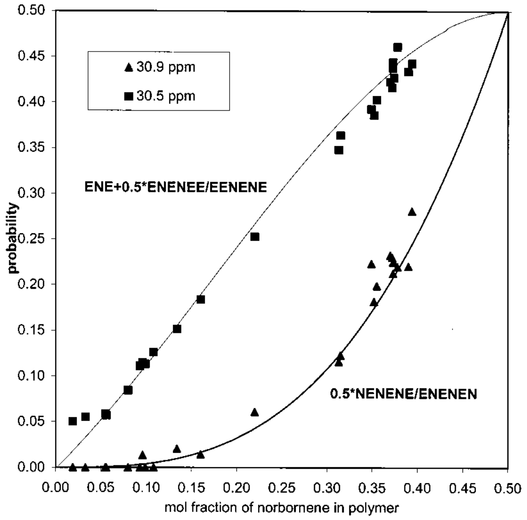


Figure 8. Copolymerization of ethene and norbornene by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO at 30 °C in toluene. Comparison of experimental peak intensity in the ^{13}C NMR spectra (▲, intensity of resonance at 30.9 ppm; ■, intensity of resonance at 30.5 ppm) with those calculated from the pentad distributions (lines). The pentad distribution is calculated by using copolymerization parameters determined from the copolymerization equation.

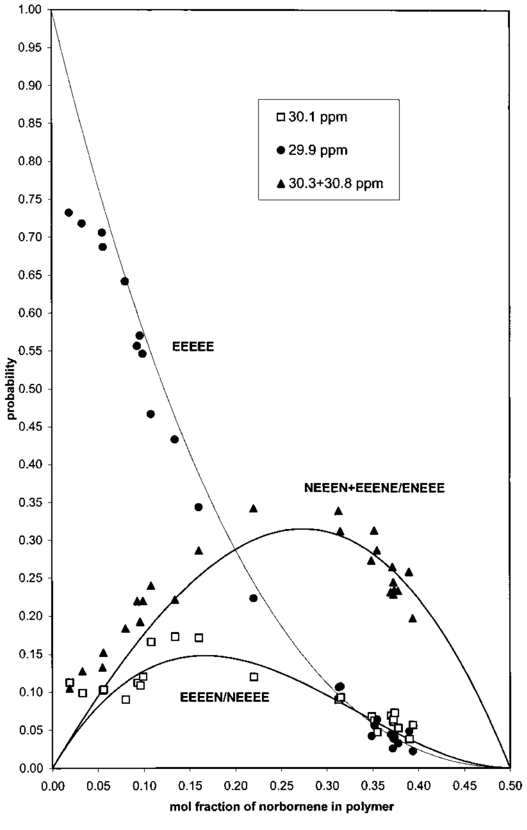


Figure 9. Copolymerization of ethene and norbornene by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$/MAO at 30 °C in toluene. Comparison of experimental peak intensity in the ^{13}C NMR spectra (▲, sum of intensities of resonances at 30.3 and 30.8 ppm; □, intensity of resonance at 30.1 ppm; ●, intensity of the resonance at 29.9 ppm) with those calculated from the pentad distributions (lines). The pentad distribution is calculated by using copolymerization parameters determined from the copolymerization equation.

Ethene-centered sequences should may give rise to seven resonances corresponding to $C_{\delta+\delta+}$, $C_{\delta\delta+}$, $C_{\gamma\delta+}$, $C_{\gamma\delta}$, $C_{\beta\delta+1}$, $C_{\alpha\delta+1}$, and $C_{\alpha\beta1}$. All these resonances are within a very small range of chemical shifts (31−29.9 ppm) and overlap to a great extent. The signal of the EEEEE pentad $C_{\delta+\delta+}$ is observed at 29.9 ppm (D1); $C_{\gamma\delta+}$ and

Table 2. Assignments for Carbons of Alternating Ethene/Norbornene Copolymers Produced by $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$/MAO at 30 °C in Toluene[a]

^{13}C chemical shifts [ppm]	assignments	sequences	peaks
48.05	C2, C3	NENEN + 0.5EENEN/NENEE = 0.5ENEN/NENE	A 2
47.35	C2, C3	EENEE + 0.5EENEN/NENEE = 0.5EENE/ENEE	A 1
42.37	C1, C4	NENEN	B 3
42.2	C1	0.5EENEN/NENEE	B 2
41.89	C1, C4	EENEE + 0.5EENEN/NENEE = 0.5EENE/EENE	B 1
33.32	C7	NENEN	C 3
33.22	C7	NENEE/EENEN	C 2
33.15	C7	EENEE	C 1
30.9	$C_{\alpha\delta+\beta}$	0.5 ENENEN/NENENE	D 6
30.8	$C_{\alpha\delta+}$	EEENE/ENEEE	D 5
30.5	C5, C6, $C_{\alpha\beta}$	ENE + 0.5ENENEE/EENENE	D 4
30.3	$C_{\alpha\delta+}$, $C_{\beta\delta+}$, $C_{\gamma\delta}$	EEENE/ENEEE + NEEEN	D 3
30.1	$C_{\delta\delta+}$, $C_{\gamma\delta+}$	EEEEN/NEEEE	D 2
29.9	$C_{\delta+\delta+}$	EEEEE	D 1

[a] All NEN sequences are features of a meso arrangement of the norbornene units; the alternating sequences are isotactic.

$C_{\delta\delta+}$ cause a resonance at 30.1 ppm (D2). The signal for $C_{\alpha\beta1}$ splits into two on the hexad level. EENENE/ENENEE adds to the signal of C5, C6 at 30.5 ppm (D4), and NENENE/ENENEN causes a resonance at 30.9 ppm (D6). The theoretical distribution of $C_{\alpha\delta+}$, $C_{\beta\delta+}$, and $C_{\gamma\delta}$ corresponds to the sum of intensities of signals at 30.8 (D5) and 30.3 ppm (D3). The peak at 30.3 ppm seems to correspond to $C_{\beta\delta+}$ and $C_{\gamma\delta}$, while that at 30.8 ppm is tentatively assigned to $C_{\alpha\delta+}$. Because of uncertainties in the deconvolution caused by signal overlapping, an unambiguous assignment is not possible. Especially experimental integral distributions of polymers containing a low amount of norbornene are less accurate. Table 2 summarizes the assignments made for the copolymers produced by $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$/MAO.

On the basis of the assignments made and the integrals detected, eqs 2−7 can be used to evaluate the triad distribution. The triads NNN and NNE/ENN are not observed, so *I*(ENE) equals the norbornene content. (Therefore, it is not shown in Figure 10.)

Copolymers produced by $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$/MAO are insoluble in hydrocarbons if the norbornene content exceeds 42−50 mol % due to the crystallinity of the alternating structure.[14] In contrast, in ethene/norbornene copolymers produced by $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO the alternating structure is disturbed by small blocks of norbornene units as the norbornene content exceeds 48 mol %. These polymers can be investigated by high-resolution ^{13}C NMR spectroscopy. Although the mechanism of copolymerizations is not totally clear yet, analysis shows the formation of odd- and even-numbered ethene sequences.[21] The additional NEENE/ENEEN pentad gives resonances of $C_{\beta\gamma1}$ and $C_{\alpha\delta1}$ which contribute to the peaks at 30.3 (D3) and 30.5 ppm (D4). At the same norbornene content the signal intensity distribution of copolymers produced by $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO differs from that found in the copolymers produced by $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$/MAO.[21]

Ethene/Norbornene Copolymers Containing Blocks. Comparison of ethene/norbornene copolymers produced by different catalysts shows that they may be divided into three subtypes according to their ^{13}C NMR spectra, but a full interpretation of the ^{13}C NMR spectra has not been achieved until now. The major differences in the subtypes reflect the ability of the different metallocenes to form blocks of norbornene of different stereoregularity. Figures 11 and 12 show representative examples at incorporation rates of 36 and 60 mol % norbornene.

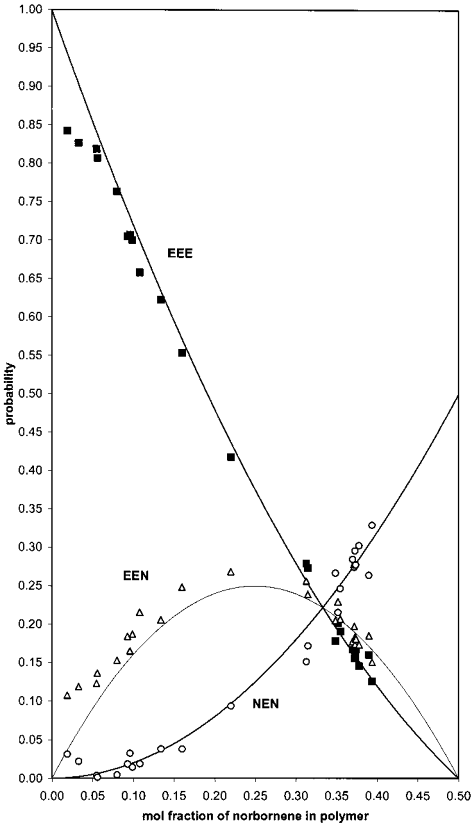


Figure 10. Copolymerization of ethene and norbornene by $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$/MAO at 30 °C in toluene. Comparison of experimental distribution of ethene centered triads and the triad distribution calculated (lines) by using the copolymrization parameters determined from the copolymerization equation.

Norbornene units can be linked in a meso or racemic manner. Figure 13 shows these structures calculated by using molecular mechanics. The different stereochemistries make the ^{13}C NMR spectra even more complicated. The spectra of hydrodimers and -trimers[8] whose structures are shown in Figures 14 and 15 are a reference as well as the chemical shifts of isolated and alternating norbornene structures in the copolymers.

Figures 16 and 17 show spectra of copolymers containing norbornene blocks and the denomination of peaks.

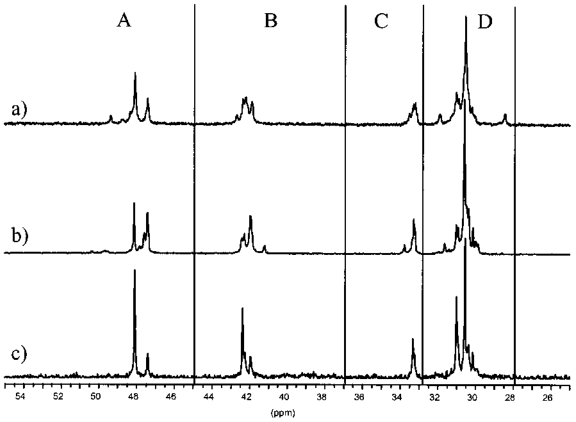


Figure 11. ^{13}C NMR spectra of ethene/norbornene copolymers containing about 36 mol % of norbornene produced by (a) *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO, (b) [$Me_2C(Cp)(Flu)$]$ZrCl_2$/MAO, and (c) [$Me_2C(3$-$MeCp)(Flu)$]$ZrCl_2$/MAO at 30 °C in toluene.

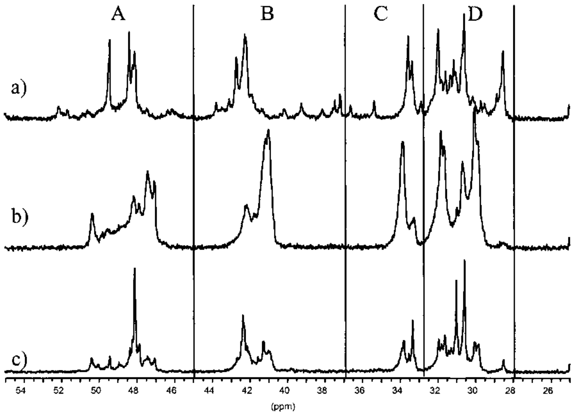


Figure 12. ^{13}C NMR spectra of ethene/norbornene copolymers containing about 60 mol % of norbornene produced by (a) *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO, (b) [$Me_2C(Cp)(Flu)$]$ZrCl_2$/MAO, and (c) [$Me_2C(3$-$MeCp)(Flu)$]$ZrCl_2$/MAO at 30 °C in toluene.

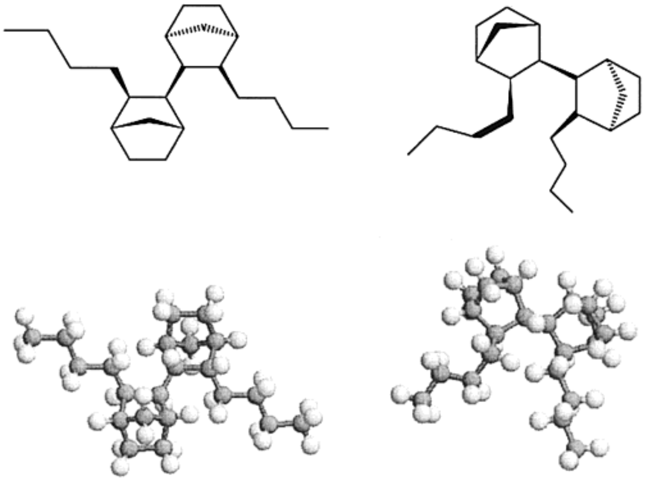


Figure 13. Structures of meso (left side) and racemic (right side) norbornene diblocks calculated by molecular mechanics (MMX force field).

Copolymers with Predominantly Meso-Linked (Isotactic) Norbornene Blocks. The catalyst system *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO shows a high selectivity for forming one type of blocks; the signals are rather sharp (Figures 16 and 17). The new signals appear at 48.3 (A5), 48.8, and 49.4 ppm (A4), and they are assigned to norbornene diblocks (ENNE tetrad). The resonance of C2 for these diblocks is assigned to the signal at 49.4 ppm by comparison to the resonances observed for alternating sequences and norbornene hydrodimers. The resonance for C3 is split on a pentad level and based

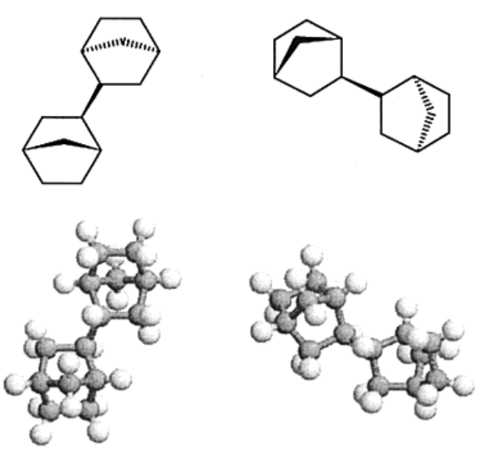


Figure 14. Structures of meso (left side) and racemic (right side) norbornene hydrodimer calculated by molecular mechanics (MMX force field).

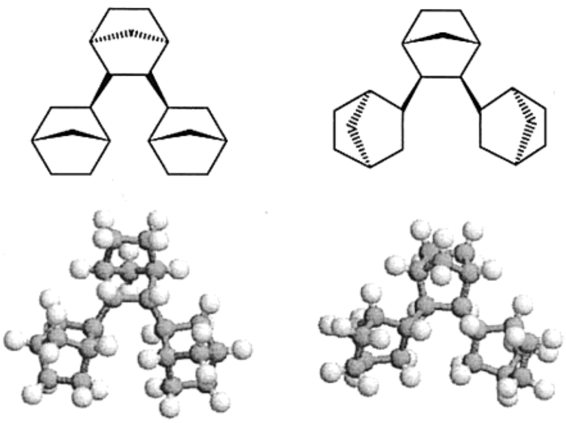


Figure 15. Structures of meso, meso (erythrodiisotactic, left side) and racemic, racemic (erythrodisyndiotactic, right side) norbornene hydrotrimer calculated by molecular mechanics (MMX force field).

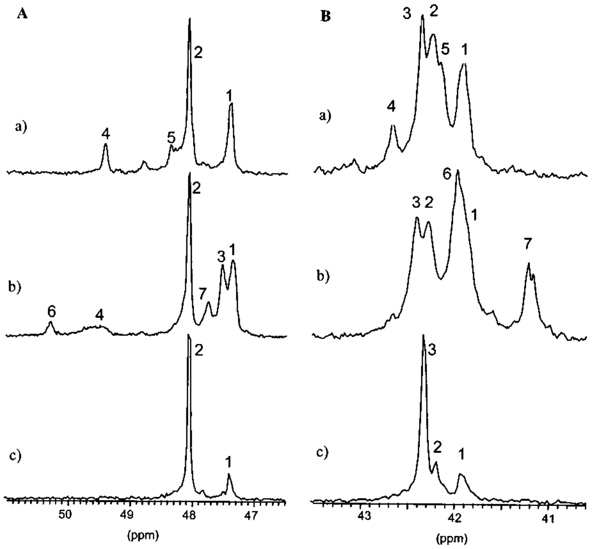


Figure 16. Regions A and B of the^{13}C NMR spectra of ethene/norbornene copolymers containing about 44 mol % of norbornene produced by (a) *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO, (b) [$Me_2C(Cp)(Flu)$]$ZrCl_2$/MAO, and (c) [$Me_2C(3$-$MeCp)(Flu)$]$ZrCl_2$/MAO at 30 °C in toluene.

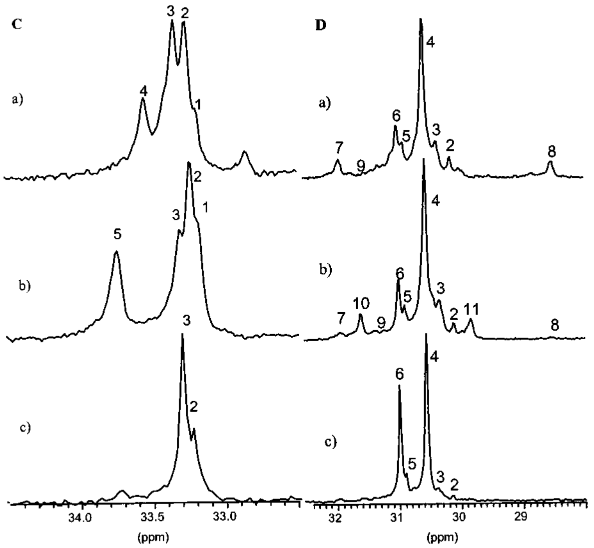


Figure 17. Regions C and D of the^{13}C NMR spectra of ethene/norbornene copolymers containing about 44 mol % of norbornene produced by (a) *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO, (b) [$Me_2C(Cp)(Flu)$]$ZrCl_2$/MAO, and (c) [$Me_2C(3\text{-}MeCp)(Flu)$]$ZrCl_2$/MAO at 30 °C in toluene.

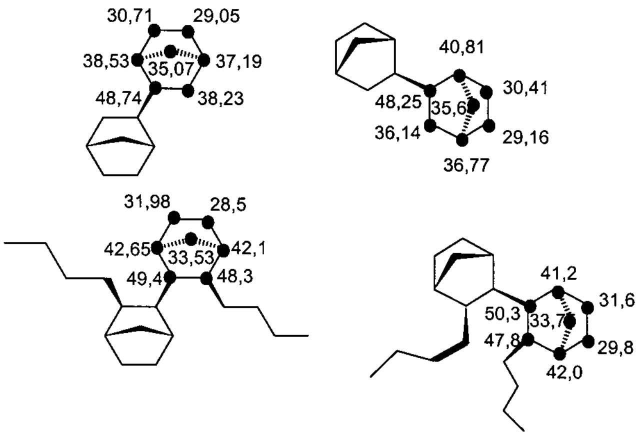


Figure 18. Comparison of the structures and chemical shifts of norbornene hydrodimers and norbornene diblocks (all chemical shifts in ppm.)

on the intensity distribution dependent on the norbornene content; C3(EENNE/ENNEE) and C3(NENNE/ENNEN) were tentatively assigned.

C1 and C4 were assigned in analogy to the hydrodimers and alternating sequences: the resonance for C1 appears at a lower field than that of C4, which in turn is similar to that of alternating structures. The resonance of C7 for norbornene diblocks (signal C4 at 33.5 ppm) is shifted to a lower field in comparison to that of C7 in ENE sequences.

The resonances of C5 and C6 in norbornene diblocks appear at 32.0 (D7) and 28.5 ppm (D8), by comparison to the hydrodimers D7 as assigned to C6 and D8 to C5. The signals of C_α neighboring norbornene blocks are shifted to resonances above 31 ppm (D9).

As known from the hydrodimers of norbornene, the difference in the chemical shifts of C2 and C3 as well as that for C1 and C4 is less in meso structures than in racemic ones (see Figure 18). So the diblocks observed in copolymers prepared by *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO are meso structures due to the relatively small splitting of the signal of C2 and C3. This is in accordance with the expected stereoregularity due to the catalyst structure and further underlined by the large difference in chemical shifts of C5 and C6 and the downfield shift of C1 and C7.

In accordance with Bergström et al., longer norbornene sequences are recognized in copolymers produced by *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO by new resonances above 52 ppm, between the four peak groups at 46 ppm, and at 40−35 ppm.

Copolymers with Predominantly Racemic-Linked (Syndiotactic) Norbornene Blocks. If a C_s symmetric catalysts precursor is capable of a highly stereoselective migratory norbornene insertion and stereoselectivity is due to enantiomorphic site control, a copolymer containing racemic linkages of the norbornene units to each other (syndiotactic blocks) will result. On the other hand, such copolymers would contain meso alternating structures for the two norbornene insertions, forming an NEN sequence that would occur at the same site of the catalyst and therefore with the same orientation of the monomer.

Copolymers produced by [$Me_2C(Cp)(Flu)$]$ZrCl_2$/MAO reflect the comparison to *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO different tacticity of the norbornene blocks as well as the lower stereoselectivity of this catalysts system. Already for copolymers containing no norbornene blocks but alternating structures an additional resonance is observed at 47.55 ppm (A3), reflecting the existence of racemic NEN sequences.[33]

Spectra of copolymers containing norbornene diblocks show two types of blocks: the meso diblocks as observed in copolymers produced by *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO and to a greater extent racemic ENNE blocks. Because of the low stereospecifity of the catalysts giving rise to racemic and meso alternating structures as well as racemic and meso diblocks, broad signals are observed (originating from rr-NENNE/ENNEN, mr-NENNE/ENNEN, rm-NENNE/ENNEN, and mm-NENNE/ENNEN).

Nevertheless, resonances for racemic diblocks could be assigned by comparison to those of the hydrodimers and meso diblocks (see Figure 18). Resonances of C2 and C3 are at a lower field than those of C2 and C3 im meso diblocks in analogy to hydrodimers, and the difference in chemical shifts also is bigger (2.5 ppm vs 1 ppm). C3 which neighbors an ethene sequence is assigned to the signal at higher field by comparison to alternating and isolated structures.

The resonance of C1 in the racemic diblock is shifted to a higher field than that of the meso diblock as in the hydrodimers. Also, the split of the resonances of C5 and C6 appearing at 31.6 and 29.8 ppm is not as large as in meso diblocks. Signals of C_α neighboring racemic diblock structures appear in the same region as C_α neighboring meso norbornene diblocks. Table 3 summarizes the assignments for copolymers containing blocks.

Tritto et al. assigned C_α neighboring norbornene diblocks to resonances of 29.7 and 29.9 ppm, C2, C3(ENNE) to 48.2, 49.3, and 50.2 ppm, and C5,C6(ENNE) to 31.5 and 31.8 ppm. No attributions for meso or racemic diblock structures were made.[19]

Because of the relatively small number of signals and the absence of overlap of the four signal groups in copolymers produced by [$Me_2C(Cp)(Flu)$]$ZrCl_2$ up to a norbornene content of 60 mol %, it is reasonable to assume that these copolymers contain only norbornene diblocks and no triblocks.

Table 3. Assignments for Carbons of Norbornene Blocks in Ethene/Norbornene Copolymers Produced by $[Me_2Si(Ind)_2]ZrCl_2$/MAO and $[Me_2C(Cp)(Flu)]ZrCl_2$/MAO at 30 °C in Toluene

catalyst	^{13}C chemical shifts [ppm]	assignts	sequences	peaks
rac-$[Me_2Si(Ind)_2]ZrCl_2$	49.4	C2	mENNE	A 4
(up to 55 mol %)	48.3.4	C3	mENNEN/ NENNE	A %
	42.65	C1	mENNE	B 4
	42.1	C4	m ENNE	B 5
	33.53	C7	mENNE	C 4
	31.98	C6	mENNE	D 7
	28.5	C5	mENNE	D 8
	31.5−31.0	$C_{\alpha\gamma\delta}$, $C_{\alpha\gamma\beta}$	(NN)E	D 9
$[Me_2C(Cp)(Flu)]ZrCl_2$	50.3	C2	rENNE	A 6
	47.8	C3	rENNE	A 7
	50.3	C2	rNENNE	I 9
	47.8	C3		I 10
	42.0	C4	rENNE	B 6
	41.2	C1	rENNE	B 7
	33.75	C7	rENNE	C 5
	31.6	C6	rENNE	D 10
	29.8	C5	rENNE	D 11
	31.5−31.0	$C_{\alpha\gamma\delta}$, $C_{\alpha\gamma\beta}$	(NN)E	D 9

For copolymers containing no NNN sequences the diad distributions can be calculated from the spectra:

$$\mathrm{NN} = 0.5\mathrm{ENN/NNE}$$

$$= \frac{0.5[I(53-46\ \text{ppm}) - I(48.05\ \text{ppm}) - I(47.55-47.35\ \text{ppm})]}{I(33-28\ \text{ppm})}$$

$$= \frac{I(34-33.4\ \text{ppm})}{I(33-28\ \text{ppm})} \qquad (8)$$

$$\mathrm{NE/EN} = 2(\mathrm{ENE} + 0.5\mathrm{ENN/NNE})$$

$$= \frac{I(53-46\ \text{ppm}) + I(48.05\ \text{ppm}) + I(47.55-47.35\ \text{ppm})}{I(33-28\ \text{ppm})}$$

$$= 2\left[\frac{2I(33.4-33\ \text{ppm}) + I(34-33.4\ \text{ppm})}{I(33-28\ \text{ppm})}\right] \qquad (9)$$

$$\mathrm{EE} = 1 - \mathrm{NE/EN} - \mathrm{NN} \qquad (10)$$

Conclusions

The microstructure of alternating ethene/norbornene copolymers is assigned for the whole ^{13}C NMR spectra, and a method to calculate the triad distributions for ethene/norbornene copolymers without norbornene blocks is described. The chemical shifts for meso and racemic norbornene diblock sequences are assigned. A method to calculate the diad distribution for copolymers containing no NNN sequences is developed.

A greater variety of copolymer structures have to be investigated to achieve a complete assignment especially for copolymers of low tacticity and high norbornene content. NMR techniques such as 2D NMR or hetero ^{1}H,^{13}C long-range correlations (two and three bonds) might help to distinguish between di- and triblocks of norbornene and to assign the stereochemistry produced by different catalysts. More ligand and catalyst systems are under investigations and will be published in the near future.

Experimental Part

All operations were carried out in an argon atmosphere using standard Schlenk, syringe, and glovebox techniques. The catalysts used were *rac*-$[Me_2Si(Ind)_2]ZrCl_2$, $[Me_2C(Cp)(Flu)]ZrCl_2$, $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$, and $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$. The synthesis has been described elsewhere.[25−27] Methylaluminoxan (MAO) (10 wt % in toluene, Witco) was stored as a solid after removal of all volatiles in a vacuum. Toluene (p.a., Riedel-de-Häen) was dried by passing through two columns, one filled with 4 Å molecular sieve and the other with a Cu catalyst (BASF R3-11). Norbornene (99%, Aldrich) was dissolved in toluene, degassed, and stirred for 24 h with triisobutylaluminum and distilled. The norbornene content was analyzed by ^{1}H NMR spectroscopy. Ethene (99.8%, Linde) was purified using two columns, one filled with 3 Å molecular sieve and the other with a Cu catalyst (BASF R3-11).

Polymerization runs were conducted in a BÜCHI 1 l glass autoclave equipped with a heat jacket. Temperature was adjusted using a thermostat with an accuracy of ± 1 °C. For a typical experiment, the reactor was evacuated at 95 °C for 1 h. Afterward, the reactor temperature was equilibrated at 30 °C. Subsequently, the reactor was charged with 500 mg of MAO, norbornene, toluene, and ethene up to a total volume of 200 mL and at the desired feed composition. The polymerization was started by addition of toluenic metallocene solution. During the reaction the ethene pressure was kept constant using a pressure controller, and ethene consumption was monitored with a mass flow meter (Brooks). Polymerization was quenched by injection of 5 mL of ethanol, and the polymer solution was stirred overnight with dilute hydrochloric acid. After separation of the organic phase and washing three times with water, the polymer was precipitated using an 8−10-fold excess of ethanol and filtered off. Finally, the polymer was dried at 60 °C in a vacuum until no more loss in weight was observed.

^{13}C NMR spectra were measured on a Bruker MSL-300 spectrometer with 75.47 MHz and at 100 °C using 200−300 mg of polymer in 3 mL of hexachloro-1,3-butadiene and 0.3 mL of 1,1,2,2-tetrachloro-1,2-dideuterioethane in 10 mm NMR tubes. All chemical shifts were referred to the solvent shift of 1,1,2,2-tetrachloroethane at 74.24 ppm (proton broad-band decoupling ^{13}C{^{1}H} NMR, pulse angle 60°, relaxation delay 6 s, acquisition delay 0.573 s). For copolymers produced by $[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$/MAO peak distributions were obtained by deconvolution.

References and Notes

(1) Kaminsky, W.; Spiehl, R. *Makromol. Chem.* **1989**, *190*, 515.
(2) Kaminsky, W.; Bark, A.; Däke, I. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Kodansha Ltd.: Tokyo, 1990.
(3) Kaminsky, W.; Bark, A.; Arndt, M. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 83.
(4) Kaminsky, W.; Bark, A.; Steiger, R. *J. Mol. Catal.* **1992**, *74*, 109.
(5) Kaminsky, W.; Noll, A. *Polym. Bull.* **1993**, *31*, 175.
(6) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.* **1993**, *194*, 3167.
(7) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1998**, *127*, 143.
(8) Arndt, M.; Engehausen, R.; Kaminsky, W.; Zoumis, K. *J. Mol. Catal. A: Chem.* **1995**, *101*, 171.
(9) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255.
(10) Lang, H. T.; Osan, F.; Wehrmeister, T. *Polym. Mater. Sci. Eng.* **1997**, *76*, 22.
(11) Arndt, M.; Kaminsky, W.; Beulich, I. In *Proceedings of the Worldwide Metallocene Conference Met′Con ′96*, Houston, TX, 1996, the Catalyst Group.
(12) Ruckartz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4869.
(13) Kaminsky, W.; Arndt, M.; Beulich, I. *Polym. Mater. Sci. Eng.* **1997**, *76*, 19.
(14) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221.
(15) Benedikt, G. M.; Goodall, B. L.; Marchant, N. S.; Rhodes, L. F. *New J. Chem.* **1994**, *18*, 105.
(16) Ruckartz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4869.
(17) Rische, T.; Waddon, A. J.; Dickinson, L. C.; MacKnight, W. J. *Macromolecules* **1998**, *31*, 1871.

(18) Bergström, C. H.; Sperlich, B. R.; Ruotoistenmäki, J.; Seppälä, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1633.
(19) Tritto, I.; Boggioni, L.; Sacchi, M. C.; Locatelli, P. *J. Mol. Catal. A: Chem.* **1998**, *133*, 139.
(20) Brekner, M.-J.; Osan, F.; Rohrmann, J.; Antberg, M. EU patent 0503422A1, Hoechst AG.
(21) Beulich, I.; Freidanck, F. W.; Schauwienold, A.-M.; Weingarten, U.; Arndt, M.; Kaminsky, W. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer Press: Berlin, 1999; p 485.
(22) Wendt, R. A.; Mynott, R.; Hauschild, K.; Ruchatz, D.; Fink, G. *Macromol. Chem. Phys.* **1999**, *200*, 1340.
(23) Tritto, I.; Boggioni, C.; Sacchi, M. C.; Locatelli, P.; Ferro, D. R.; Provasoli, A. *Macromol. Rapid Commun.* **1999**, *20*, 279.
(24) McKnight, A. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 2816.
(25) Razavi, A.; Ferrara, J. *J. Organomet. Chem.* **1992**, *435*, 299.
(26) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255.
(27) Spaleck, W.; Antberg, M.; Aulbach, M.; Bachmann, B.; Dolle, V.; Haftka, S.; Küber, F.; Rohrmann, J.; Winter, A. In *Ziegler-Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer Press: Berlin, 1995; p 83 and references therein.
(28) While the revised version of this manuscript was in preparation Fink et al. were able to achive a triad analysis of ethene/norbornene copolymers.[22]
(29) They assigned structures which coupled with new signals in the ^{1}H NMR sprectrum as norbornene diads. Nevertheless, no details were given if C2(NN) and C4(NN) coupled over three bonds with hydrogens at Cα(NNE), or if C3(NN) coupled over two bonds with hydrogens at Cα(NNE), and if C1(NN) did not couple with hydrogens at Cα(NNE), so that these signals were only diads and not triads.
(30) While the revised version of this manuscript was in preparation they revised some of their assignments.[23]
(31) For the calculation of the amount of norbornene centered triads also the integrals of the resonances of C1, C4, or C5, C6 or C7 may be used.
(32) For calculations $r_E{}^B$ is set to 500.
(33) While the revised version of this manuscript was in preparation Waymouth et al. described a similar effect for ethene/norbornene copolymers produced by constrained geometry type of catalysts.[24]

MA981813Z