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Synthesis of novel metallacyclic zirconocene complexes from ω-alkenyl-functionalized zirconocene dichloride complexes and their use in the α-olefin polymerization

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Abstract

Novel metallacyclic zirconocene complexes were prepared by reacting ω-alkenyl substituted zirconocene dichloride complexes with two equivalents of *n*-butyllithium. The factor determining the reaction course and the structure of the respective metallacycle formed is the chain length of the alkenyl group. After activation with methylaluminoxane the metallocene dichloride complexes and the derived metallacyclic derivatives are excellently suited for ethylene polymerization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metallacycles; Zirconocene complexes; Cyclization; Catalysis; Ethylene polymerization

1. Introduction

With their defined molecular structure and their high polymerization activity metallocene complexes with Group IV metals in combination with methylaluminoxane (MAO) have become more and more important over the last few years as catalysts for the polymerization of α-olefins [1–17].

Next to various π-ligands such as cyclopentadienyl, indenyl and fluorenyl, also substituents on these ligands have a strong influence on the polymerization characteristics of the respective metallocene catalyst system [18–21]. Important substituents are ω-alkenyl groups which not only exert a steric effect on the accessibility of the polymerization inducing catalytic center but also are incorporated into the polyolefin in a comonomer-like fashion, thereby heterogenizing the alkenyl functionalized catalyst [21–24].

Metallocene complexes with an activated metal center are not only suitable for the polymerization of α-olefins but also give access to a variety of reactions. This activation, for instance, can be accomplished by a transition from oxidation state four to oxidation state two [25–30] or by introducing reactive ligands such as a hydrido ligand [31–33]. Whereas intermolecular hydrozirconation reactions of alkenes with the Schwartz reagent [32,33] proceed quantitatively, this type of reaction is of only limited value for the intramolecular hydrozirconation of π-ligand-bound ω-alkenyl groups because of their significantly lower yields [21,24].

An efficient method for synthesizing metallacyclic zirconocene complexes derived from alkenyl substituted zirconocene dichloride complexes would indeed be desirable since metallacycles are of high value for catalytic olefin polymerization [20,34]. So far only a method using sodium amalgam for the synthesis of metallacycles from *rac*-dimethylsilyl bridged bis(4-pentenylindenyl) metal dichloride complexes is known [35].

We now describe a quantitative method of synthesis based on an organometallic reagent that offers a broad access to such metallacycle. It was of particular interest to investigate the effect of the length of the alkenyl group on the reaction course and the structure of the produced metallacycle.

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2. Results and discussion

2.1. Synthesis of metallacyclic zirconocene complexes

In this paper, metallacycles are defined as metallocene complexes with a substituent on the π-ligand which possesses a σ-bond to the central metal.

The newly developed method of synthesis is based on the reaction of ω-alkenyl-substituted zirconocene dichloride complexes with two equivalents of *n*-butyllithium. When bis(allylcyclopentadienyl)zirconium dichloride (**1**) (Fig. 1) [36] is used, this reaction yields the zirconocene dibutyl complex **1a** as an intermediate product which is stable for several minutes in solution at low temperatures (−40 °C). The unsubstituted parent compound was characterized spectroscopically [25].

The dibutyl complex eliminates *n*-butane via a β-H shift [37,38] and the formation of a reactive (η^2-butene) complex can be concluded from spectroscopic investigations on similar complexes [39]. In the reaction of Cp_2ZrCl_2 with two equivalents of *n*-butyllithium, '$Cp_2ZrC_4H_8$' is formed as an intermediate that can be trapped with trimethylphosphane [26,40,41]. The zirconocene complexes used in this series are assumed to form a metastable η^2-butenyl-η^2-alkenyl-Zr moiety (**1b**). The decisive reaction step in the formation of a metallacycle is probably a 2+2+2 cycloaddition leading to a zirconacyclopentane moiety. With bis(allylcyclopentadienyl)zirconium dichloride (**1**) [36] the zirconacyclopentane structure (**1c**) is most likely to be formed by the integration of the 1-butene ligand into the ring structure. Obviously because of the close proximity of the allyl group on the second cyclopentadienyl ligand, the reaction does not stop at this stage but it seems to proceed with a CH-activating reaction in which a terminal hydrogen atom of the allyl group is transferred to a methylene group in an α-position to the central metal. The metallacycle **2** is obtained in quantitative yield; its structure could be verified by one- and two-dimensional NMR spectroscopy (see Section 2.2).

It is important to note that only one stereoisomer is formed in this multi-step reaction despite the presence of several centers of asymmetry.

In the reactions of the bis(alkenylcyclopentadienyl)zirconium dichloride complexes **3**–**5** [42], having a longer spacer unit between the double bond and the cyclopentadienyl ligand (C_2 to C_4), the metastable η^2-butene-η^2-alkenyl-Zr moiety (**3b**–**5b**) is most likely to be formed in a manner analogous to **1**.

However, presumably for steric reasons, the reactions of the metallocene complexes with C_2 to C_4 spacers then seem to proceed through a 1-butene elimination and the double bond of the alkenyl group on the second cyclopentadienyl ligand coordinates to the now free coordination site (**3c**–**5c**). This coordination of the alkenyl group with elimination of 1-butene can also be interpreted as a displacement reaction. Such displacement reactions of 1-butene from the coordination sphere of zirconium by various π-donors (e.g. ethylene, alkynes, trimethylphosphane) have been described a number of times for unsubstituted zirconocene complexes [43,44].

The proposed metallocene intermediates **3c** and **4c** with C_2 and C_3 spacers react with the formation of a C_s-symmetrical zirconacyclopentane structure to the metallacycles **6** and **7** (Fig. 2).

In contrast to the metallacycle **1c**, with its bridge from the metallacyclopentane structure to the π-ligand on the β-carbon to the zirconium, the metallacycles **6**–**8** have bridges on the α-carbon atom. It can be assumed that the differing bridge positions are due to steric requirements, in particular to avoid excessive ring strain. Unbridged metallacyclopentane complexes, for example $Cp_2ZrC_4H_8Me_2$, with their non-existent steric

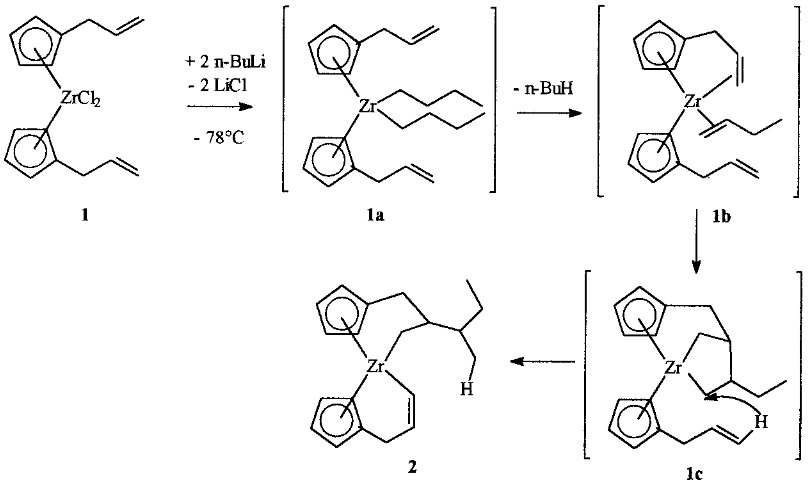


Fig. 1. Proposed reaction sequence for the formation of metallacycle **2** from bis(allylcyclopentadienyl)zirconium dichloride (**1**).

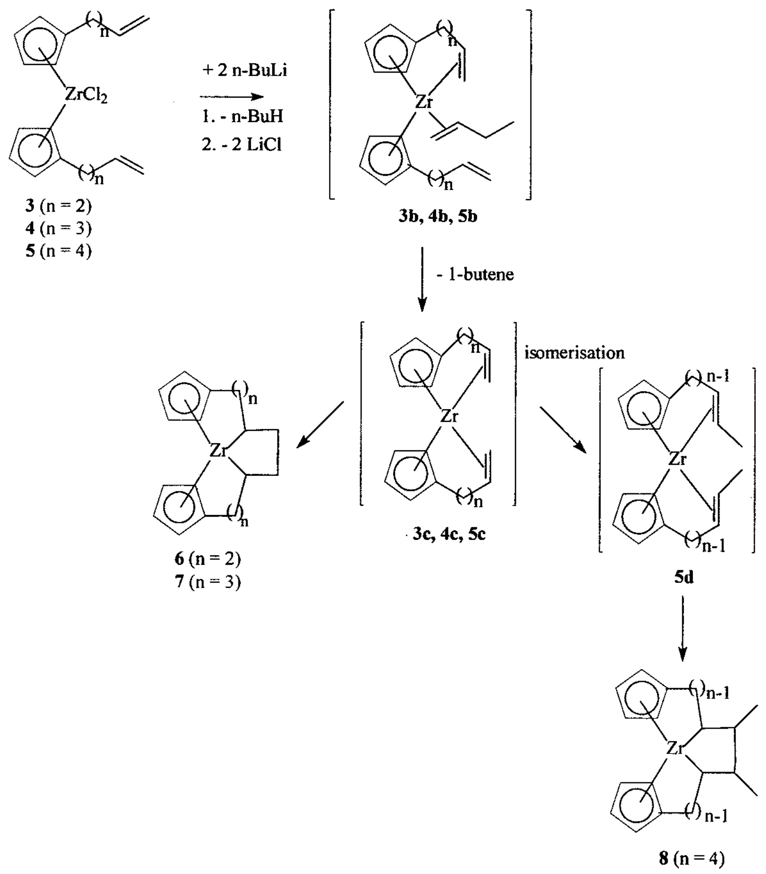


Fig. 2. Proposed reaction sequence for the formation of metallacycles **6**–**8**.

effects, always form mixtures of isomers with branching (methyl) in the α- and β-position [45,46].

With the proposed metallocene intermediate **5c**, having a C_4 spacer, an isomerization of the terminal double bond in hex-5-enyl groups to hex-4-enyl groups with the formation of the proposed **5d** seems to occur prior to the reaction of the zirconacyclopentane structure to the metallacycle **8**. This type of double bond isomerization is facilitated in the coordination sphere of transition metals and found in a number of reactions catalyzed by transition metals [47]. The isomerization presumably proceeds via the π-allyl hydride mechanism, involving a metal-induced intramolecular 1,3-hydrogen shift [48,49].

Because of the proposed isomerization the zirconacyclopentane structure of metallacycle **8** has two methyl groups in positions 3 and 4 of the zirconacyclopentane structure. An analogous structure was shown in a substituted titanocene complex, prepared by reduction of the associated titanium dichloride complex with magnesium in tetrahydrofuran [50].

Besides the symmetrical bis(cyclopentadienyl)zirconium dichloride complexes, other complexes of the type (alkenylcyclopentadienyl)(indenyl)zirconium dichloride were reacted with two equivalents of *n*-butyllithium. The (alkenylcyclopentadienyl)(indenyl)zirconium dichloride complexes **9**–**12** with mixed substituents and C_1 to C_4 spacers were prepared in known fashion by reacting the respective alkenylcyclopentadienyl lithium derivatives with indenylzirconium trichloride [51] in diethyl ether.

When the metallocene dichloride complexes **9**–**12** with mixed substituents are treated with two equivalents of *n*-butyllithium, the reaction is likely to proceed in the formation of a metastable η^2-1-butene-η^2-alkenyl-zirconium moiety (**9b**–**12b**), as with the symmetrical bis(alkenylcyclopentadienyl)zirconium dichlorides **1** and **3**–**5** (Fig. 3).

Since the second π-ligand has no alkenyl group, in contrast to the bis(alkenylcyclopentadienyl)zirconium dichloride complexes **3**–**5** with C_2 to C_4 spacers, no displacement of 1-butene by the alkenyl group can occur. Furthermore, because of the missing second allyl group, the reaction of (allylcyclopentadienyl)(indenyl)zirconium dichloride (**9**) with *n*-butyllithium does not go further in comparison with bis(allylcyclopentadienyl)zirconium dichloride (**1**) where a terminal hydrogen atom is probably transferred in a CH-activation reaction to the zirconacyclopentane structure. Therefore most likely, in the (allylcyclopentadienyl)(indenyl)zirconium dichloride (**9**) with mixed substituents a completely different metallacyclic structure as compared

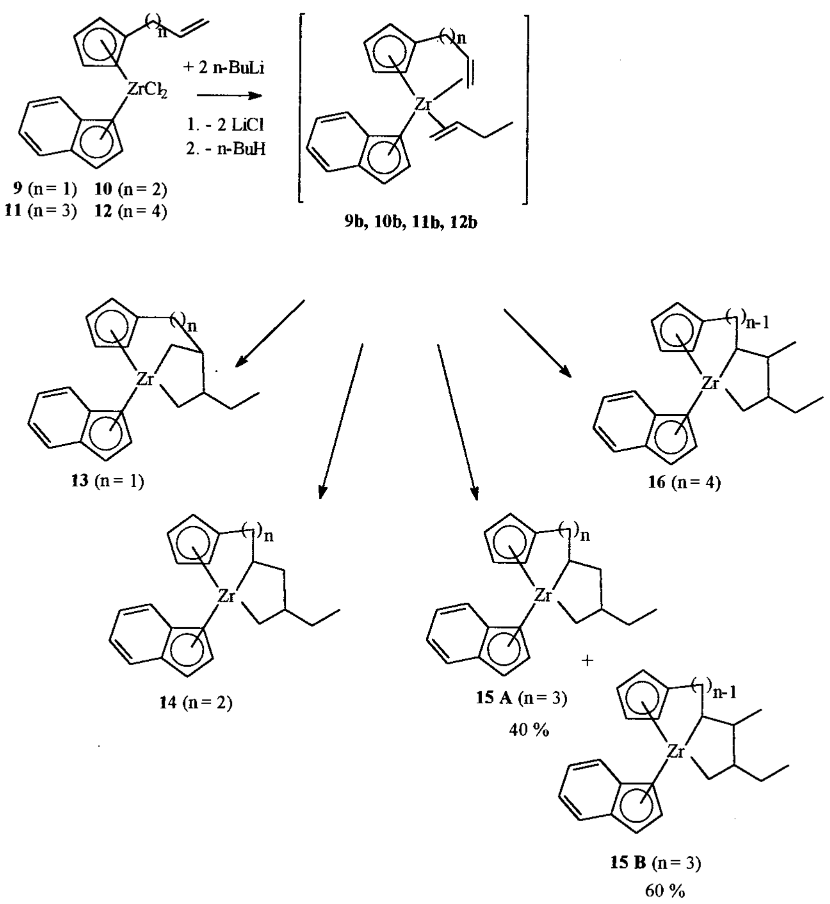


Fig. 3. Proposed reaction sequence for the formation of metallacycles **13**–**16**.

with the symmetrical bis(alkenylcyclopentadienyl)zirconium dichloride (**1**) is obtained.

As with metallacycle **2**, the metallacycle **13** (both C_3-alkenyl groups) is bridged from the metallacyclopentane structure to the π-ligand on the β-carbon atom to zirconium. The metallacycles **14**–**16** (C_4- to C_6-alkenyl precursor) have, as do their symmetrical metallacyclic analogs **6**–**8**, the bridges at the α-carbon atoms.

As with metallacycle **8**, in intermediate **11b** an isomerization of the terminal double bond (pent-4-enyl group) to a pent-3-enyl group and thus the formation of metallacycle **15B** seem to occur to the extent of 60%, prior to the formation of the zirconacyclopentane structure. The structural isomer **15A**, where no double bond isomerization occurs, is formed to the extent of 40%.

In intermediate **12b**, presumably because of the different steric situation, the proposed isomerization of the terminal double bond (hex-5-enyl) to a hex-4-enyl group prior to the formation of the zirconacyclopentane structure with metallacycle **16** proceeds to 100%.

*2.2. Spectroscopic characterization of the metallocene complexes **1**–**16***

The metallocene complexes **1**–**16** were characterized by ^{1}H- and ^{13}C-NMR spectroscopy. The data obtained are listed in Table 2. The ^{1}H- and ^{13}C-NMR spectra of metallocene complex **2** will be discussed as an example. The assignments of the individual proton and carbon shifts of metallocene complex **2** are supported by 2D-^{1}H, ^{1}H-COSY45 NMR experiments and 2D-^{1}H, ^{13}C heteronuclear shift correlation experiments.

Fig. 4 shows the ^{1}H-NMR spectrum of **2**. The eight cyclopentadienyl protons H^1–H^4 and H^9–H^{12} give rise to eight different resonance signals at $\delta = 6.44$, 6.17, 5.69, 5.67, 5.41, 5.11, 5.09 and 5.01 ppm. This indicates the presence of a chiral metallocene complex caused by the two different metallacyclic structures around the metal. The resonance signals from protons H^6–H^8 of the allylidene bridge are observed as multiplets at $\delta =$ 7.39 (H^7; β-CH) and 7.02 ppm (H^8; α-CH) from the two protons H^7 and H^8 of the double bond, and at $\delta = 3.35$ and 3.15 ppm from the geminal protons H^{6a} and H^{6b} of the γ-methylene group. The geminal $^2J(^1H^1H)$ coupling constant of these two protons is 17.5 Hz, but with these two doublets being further split to a multiplet by a small coupling to the proton on the β-CH group.

The resonance signals from the protons on the second metallacyclic moiety appear as multiplets at $\delta =$ 2.75 and 2.25 ppm from the γ-protons H^{14a} and H^{14b}, at

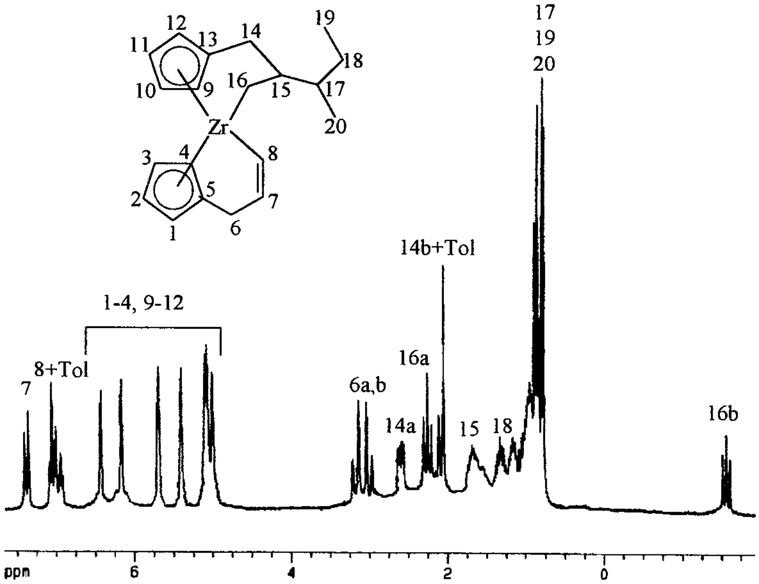


Fig. 4. ^{1}H-NMR spectrum of metallocene complex **2** (in C_6D_6, 25 °C); Tol = toluene.

$\delta = 1.75$ ppm from proton H^{15} on the β-methine group and at $\delta = 2.43$ and -1.36 ppm from protons H^{16a} and H^{6b} on the α-carbon atom.

The 2-butane group on the second metallacyclic moiety shows the following resonance signals: the protons from the two methyl groups H^{19} and H^{20} give rise to a triplet ($^3J(^1H^1H)$ coupling = 6.9 Hz) at $\delta = 0.86$ ppm and a doublet ($^3J(^1H^1H)$ coupling = 6.4 Hz) at $\delta = 0.78$ ppm. The protons H^{17}, H^{18a} and H^{18b} give rise to multiplets at $\delta = 1.14$, 1.33 and 0.98 ppm.

Fig. 5 shows the ^{13}C-NMR spectrum of metallacycle **2**. The presence of eight different tertiary carbon atom resonance signals C^1–C^4 and C^9–C^{12} for the two cyclopentadienyl ligands at $\delta = 103.1$–117.1 ppm is due to the chiral structure of **2**. The resonance signals from the associated quaternary carbon atoms C^5 and C^{13} are observed at $\delta = 142.0$ and 138.7 ppm. The resonance signals from the carbon atoms on the allylidene bridge are found at 183.3 (C^8; α-CH), 163.3 (C^9; β-CH) and 37.4 ppm (C^6; γ-CH_2). The downfield shift of the α-CH group C^8 is significant for a double bond system directly bound to the metal [34].

The carbon atoms of the second metallacyclic moiety C^{14}–C^{16} give rise to resonance signals at $\delta = 61.2$ (C^{16}; α-CH_2), 57.6 (C^{15}; β-CH) and 33.3 ppm (C^{14}; γ-CH_2). The associated 2-butane group shows resonance signals at $\delta = 42.0$ (C^{17}; CH), 27.5 (C^{18}; CH_2), 15.7 (C^{19}; CH_3) and 12.6 ppm (C^{20}; CH_3).

2.3. Polymerization of ethylene

The synthesized metallocene complexes are suitable precursors for the homogeneous polymerization of ethylene. Activation is achieved by addition of a 3000-fold molar excess of MAO. The formation of the active catalyst can be observed by a color change.

Table 1 summarizes the polymerization activities of the activated metallocene complexes, the number average of the molecular weight $\bar{M}_n$, the weight average of the molecular weight $\bar{M}_w$, the viscosity average of the molecular weight $\bar{M}_\eta$, the centrifuge average of the molecular weight $\bar{M}_z$ and the polydispersity index $\bar{D}$ of the polymers obtained.

*2.3.1. Effect of the spacer chain length on the polymerization characteristics of the symmetrically substituted metallocene dichloride complexes **1** and **3**–**5** and the derived metallacycles **2** and **6**–**8***

The length of the spacer chain between the π-ligand and the double bond strongly influences the polymerization characteristics of the metallocene complexes prepared. Fig. 6 shows a comparison between the polymerization activities in the homogeneous polymerization of the ω-alkenyl-substituted bis(cyclopentadienyl)zirconium dichloride complexes **1**, **3**–**5** and the derived metallacycles **2**, **6**–**8**. After activation with MAO the metallacyclic complexes exhibit, in comparison to the respective metallocene dichloride complexes with the same spacer chain lengths, a lower polymerization activity (35–80%). This decreased activity could be caused, on the one hand, by the sterically more demanding branched alkyl substituents on the metallacycles which exert a shielding effect on the catalytic center. On the other hand, this could also be due to the formation of a zwitterion in the activation of the metallacycles with MAO which results in a smaller separation between the MAO counter ion and the active cationic catalytic center. [52]. A third reason for the lower activities of the metallacycles could be a differ-

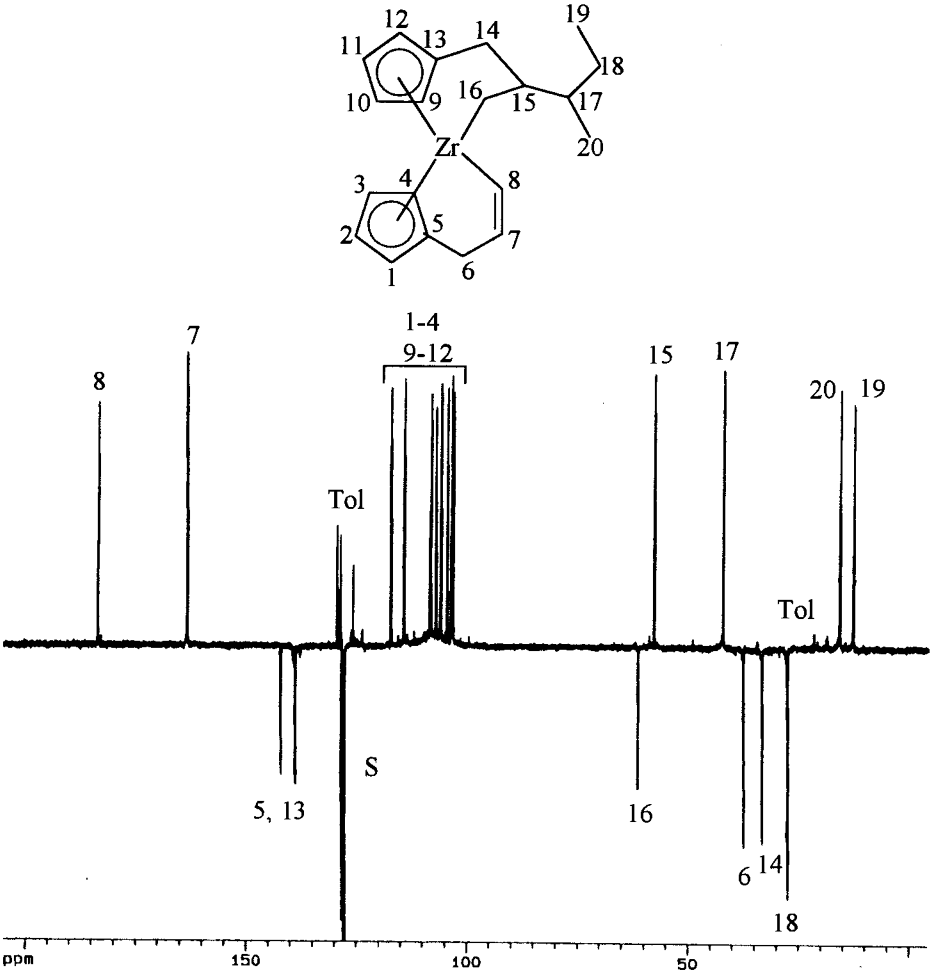


Fig. 5. *J*-modulated $^{13}C\{H\}$-NMR spectrum of metallocene complex **2** (in C_6D_6, 25 °C); Tol = toluene, S = solvent benzene-d_6.

ence in the activation efficiency due to the different activation mechanism compared to the metallocene dichloride complexes.

With increasing length of the carbon atom spacer chain from C_1 to C_3 the polymerization activity also increases, both in the metallocene dichloride complexes **1**, **3** and **4** and in the metallacycles **2**, **6** and **7**. Longer alkenyl and alkyl substituents could lead to an increased separation of the metallocene monoalkyl cation and the MAO anion.

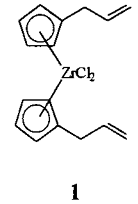
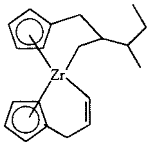
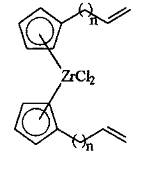
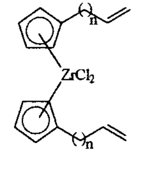
Going from a carbon atom spacer length C_3 to C_4 the polymerization activity only drops slightly in the metallocene dichloride complexes but strongly in the case of the metallacycles. This significant decrease is presumably caused by the highly branched (through the methyl groups) nature of the alkyl group.

Fig. 7 shows the molecular weights of the polyethylenes obtained with the alkenyl-substituted metallocene complexes and the derived metallacycles. Both for the metallocene dichloride complexes **1**, **3** and **4** and for the metallacycles **2**, **6** and **7** the molecular weights of the polyethylenes increase with increasing length of the carbon atom spacer chain from C_1 to C_3. The extension of the alkyl spacers seems to lead to a hindered β-H elimination and thus to higher molecular weights in the polymerization.

*2.3.2. Effect of the spacer chain length on the polymerization characteristics of the metallocene dichloride complexes **9–12** with mixed substituents and the derived metallacycles **13–16***

Fig. 8 compares the polymerization activities of the metallocene dichloride complexes **9**–**12** with those of the corresponding metallacycles **13**–**16**. The metallocene dichloride complexes **11** and **12** and the derived metallacycles **15** and **16** with a C_3 or C_4 spacer show significantly higher polymerization activities than the metallocene dichloride complexes **9** and **10** and the derived metallacycles **13** and **14** with a C_1 or C_2 spacer. This behavior is not comparable with the increase in the polymerization activity with increasing spacer chain lengths in the symmetrical bis(alkenyl)dichloride complexes and the derived metallacycles (see Section 2.3.1). Exchange of an ω-alkenyl-substituted cyclopentadienyl

Table 1
Summary of the polymerization experiments[a] and polymer properties

g PE mmol Zr·h	Activity[b)] [———]	HT-GPC[c)]: $\overline{M}_n$ $\overline{M}_w$ $\overline{M}_z$ $\overline{M}_\eta$ in [kg/mol] $\overline{D}$	DSC[d)] T_m [°C] ΔH_m [J/g] α[%][d)]
 **1**	117200	500 989 2244 903 2.0	140.2 157.1 54.2
 **2**	41700	337 991 4065 866 2.9	139.8 147.7 50.9
 **3** (n = 2)	150500	609 1119 2557 1019 1.8	135.4 141.3 48.7
 **4** (n = 3)	157800	871 3287 39842 2323 3.8	138.6 141.6 48.8

ligand for an unsubstituted indenyl ligand does not seem to be of significant influence on the polymerization characteristics.

Metallacycle **15** shows, after activation with MAO, with approximately 327 kg of polyethylene per hour and mmol of zirconium, the highest polymerization activity among all the metallocene catalysts investigated.

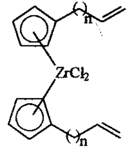
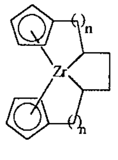
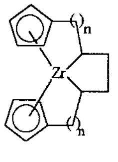
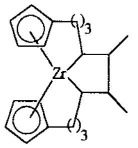
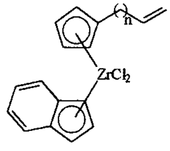
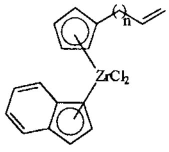
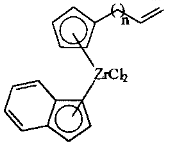
The molecular weights of the polyethylenes prepared with the metallocene dichloride complexes **9**–**12** and the derived metallacycles **13**–**16** are graphically illustrated in Fig. 9. In contrast to the molecular weights of the polyethylenes obtained with the symmetrical bis(alkenylcyclopentadienyl)zirconium dichlorides and the derived metallacycles, no correlation with the chain length can be discerned in the molecular weights of the polyethylenes obtained with the metallocene complexes with mixed substituents.

3. Experimental

3.1. NMR spectroscopy

The NMR spectra were recorded with a Bruker ARX 250 spectrometer. The organometallic samples were prepared under Ar and measured at 25 °C. The chemical shifts in the ^{1}H-NMR spectra refer to the residual solvent proton signal ($\delta = 7.24$ ppm for $CHCl_3$, $\delta = 7.15$ ppm for benzene) and in the ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ ppm for $CHCl_3$-d_1, $\delta = 128.0$ ppm for benzene-d_6).

Table 1 (*Continued*)

 **5** (n = 4)	152200	465 2962 151550 1598 6.4	136.9 139.3 48.0
 **6** (n = 2)	105300	582 2686 51557 1792 4.6	137.8 141.4 48.8
 7 (n = 3)	123800	640 1004 1679 943 1.6	136.9 152.6 52.6
 **8** (n = 4)	59900	398 978 3815 855 2.5	137.2 150.4 51.9
 **9** (n = 1)	84900	370 991 2451 894 2.7	139.3 159.6 55.0
 **10** (n = 2)	111200	271 930 2433 824 3.4	138.4 147.0 50.7
 **11** (n = 3)	310600	589 1901 10420 1553 3.2	139.3 136.5 47.1

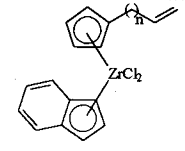
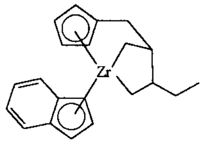
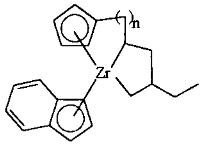
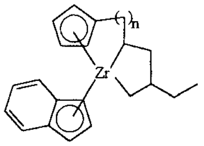
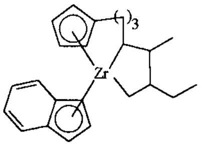
3.2. Mass spectrometry

Routine measurements were performed with a Varian MAT CH7 instrument (direct injection, electron impact ionization 70 eV). GC/MS spectra were recorded with a Varian 3700 gas chromatograph in conjunction with a Varian MAT 312 mass spectrometer.

3.3. General procedure for the synthesis of the symmetric metallocene dichloride complexes *1* and *3*–*5*

12.6 ml (20.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) was added to a solution of 20.0 mmol of the respective ligand precursor in 150 ml of Et_2O at −78 °C. Zirconium tetrachloride (2.4 g, 10.0 mmol)

Table 1 (*Continued*)

 **12** (n = 4)	296500	908 3305 58888 2256 3.6	138.1 150.5 51.9
 **13** (n = 1)	35800	449 1163 5780 1003 2.6	138.4 153.0 52.8
 **14** (n = 2)	68100	855 589 173350 3374 6.9	136.9 137.9 47.8
 **15**[e] (n = 3)	327300	607 2431 32720 1795 4.0	137.8 144.0 49.7
 **16** (n = 4)	163900	721 3384 64575 2220 4.7	137.8 151.9 52.4

[a] T_p = 60 °C; solvent: 500 ml of n-pentane; 10 bar ethylene pressure; 1 h polymerization time.

[b] [M]/[Al] = 1:3000.

[c] $\overline{M}_n$ = number average of molecular mass
$\overline{M}_w$ = weight average of molecular mass
$\overline{M}_z$ = centrifuge average of molecular mass
$\overline{M}_\eta$ = viscosity average of molecular mass
$\overline{D}$ = $\overline{M}_w$/ $\overline{M}_n$ = polydispersity

[d] Degree of crystallinity with regard to the enthalpy of fusion of 100 % crystalline polyethylene.

[e] Product mixture from **15A** (shown) and **15B**.

was then added to the reaction at −78 °C and the mixture was stirred overnight at room temperature (r.t.). The suspension was filtered through Na_2SO_4 and the solvent was evaporated in vacuo. The residue was washed twice with *n*-pentane and solvent residues were removed in vacuo. The metallocene dichloride complexes were obtained with yields of **1**: (2.68 g) 72%; **3**: (3.52 g) 88%; **4**: (3.60 g) 84%; **5**: (3.47 g) 76%. The complexes were characterized by their NMR spectra (Table 2) and their mass spectra (Table 3).

*3.4. General procedure for the synthesis of the metallocene dichloride complexes **9–12** with mixed substituents*

6.3 ml (10.0 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane) was added to a solution of 10.0 mmol of the respective ligand precursor in 150 ml of Et_2O at −78 °C and the reaction mixture was stirred at r.t. for 6 h. Indenylzirconium trichloride (3.1 g, 10.0 mmol) was then added to the reaction at −78 °C and the

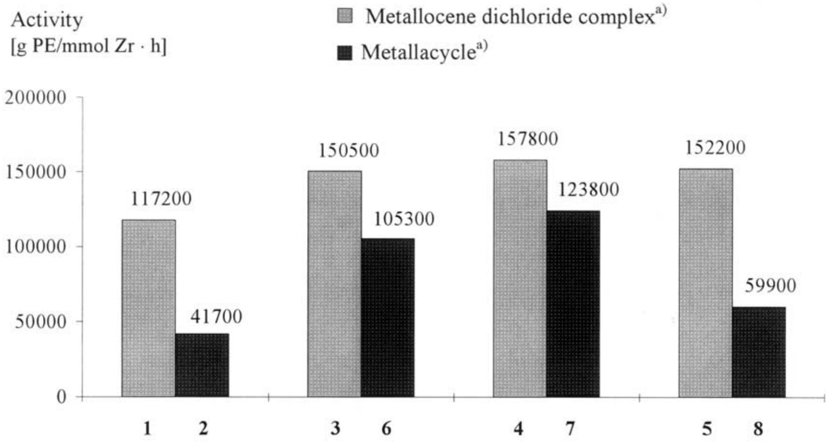


Fig. 6. Comparison of the polymerization activities of metallocene dichloride complexes **1** and **3**–**5** and the analogous metallocene complexes **2** and **6**–**8**. [a] Homogeneous polymerization in *n*-pentane at 60 °C (1 h) after activation with MAO (Zr–Al = 1:3000).

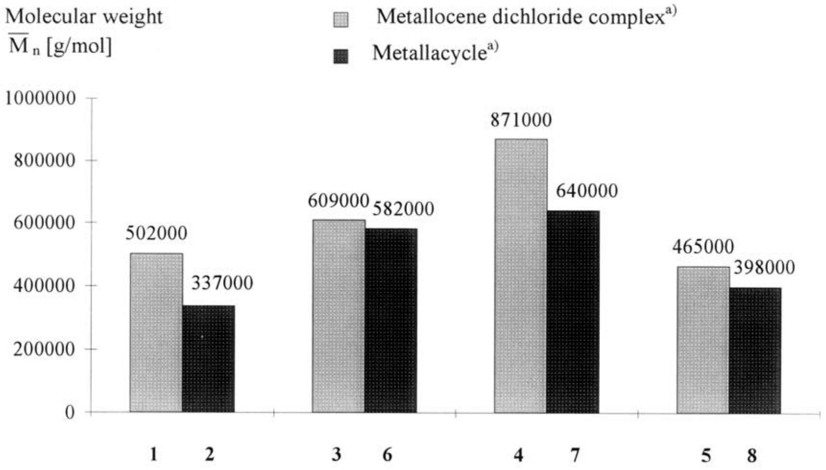


Fig. 7. Comparison of the molecular weights of polyethylenes prepared with the metallocene dichloride complexes **1** and **3**–**5** and the analogous metallocene complexes **2** and **6**–**8**. [a] Homogeneous polymerization in *n*-pentane at 60 °C (1 h) after activation with MAO (Zr–Al = 1:3000).

mixture stirred overnight at r.t. The solvent was evaporated in vacuo to a volume of 50 ml, the suspension filtered through Na_2SO_4 and the residue extracted with CH_2Cl_2. The solution was concentrated and the product crystallized at −20 °C. The metallocene dichloride complexes were obtained with yields of **9**: (2.03 g) 53%; **10**: (2.81 g) 71%; **11**: (2.83 g) 69%; **12**: (3.14 g) 74%. The complexes were characterized by their NMR spectra (Table 2) and their mass spectra (Table 4).

3.5. General procedure for the synthesis of the metallocene complexes 2, 6–8 and 13–16

3.8 ml (6.0 mmol) of *n*-butyllithium was added to a solution of 3.0 mmol of the respective metallocene dichloride complex in 50 ml of toluene at −78 °C. The mixture was warmed to r.t. for 6 h and stirred overnight. For work-up the mixture was filtered through Na_2SO_4 and the solvent evaporated in vacuo. The metallocene complexes were obtained as orange–red oils or solids with yields of **2**: (1.02 g) 95%; **6**: (0.93 g) 94%; **7**: (1.02 g) 95%; **8**: (1.08 g) 93%; **13**: (1.01 g) 92%; **14**: (1.12 g) 98%; **15**: (1.01 g) 85%; **16**: (1.16 g) 94%. M.p. (dec.) (°C) — **2**: 210–212; **6**: 270–272; **7**: 239–242; **8**: 248–250. Found (calc.): $C_{20}H_{26}Zr$ (**2**): C, 65.00 (67.17); H, 7.32 (7.33)%; $C_{20}H_{26}Zr$ (**7**): C, 66.30 (67.17); H, 7.57 (7.33)%; $C_{22}H_{26}Zr$ (**14**): C, 67.58 (69.23); H, 6.58 (6.87)%; $C_{24}H_{30}Zr$ (**16**): C, 69.51 (70.04); H, 7.22 (7.38)%. The complexes were characterized by their NMR spectra (Table 2). The mass spectra ($E_i = 70$ eV) of the complexes did not show the molecular ion but the expected complex fragments.

3.6. Characterization of metallocene complexes 1–16 by NMR spectroscopy

NMR spectroscopy data of metallocene complexes **1**–**16** are summarized in Table 2.

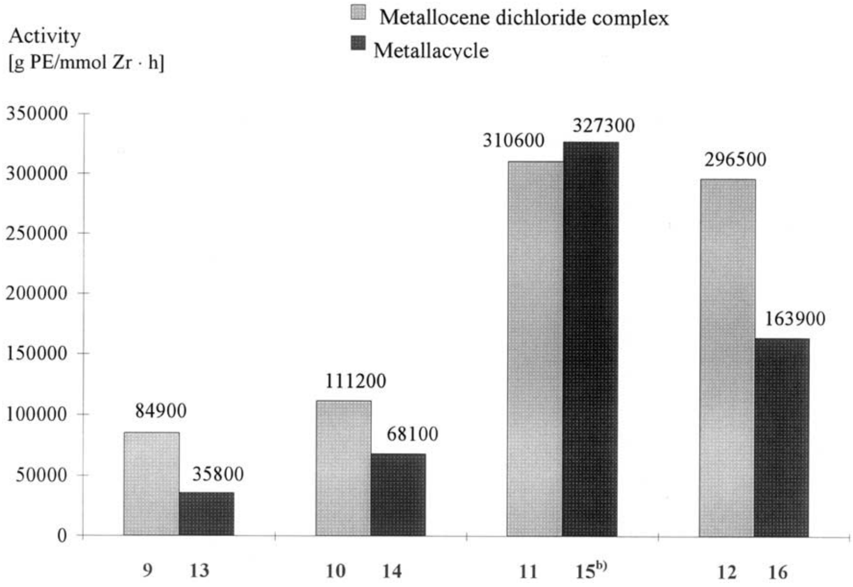


Fig. 8. Comparison of the polymerization activities of the metallocene complexes **9**–**12** with mixed substituents with the activities of the corresponding metallacycles **13**–**16**. [a] Homogeneous polymerization in *n*-pentane at 60 °C (1 h) after activation with MAO (Zr–Al = 1:3000); [b] product mixture from **15A** and **15B**.

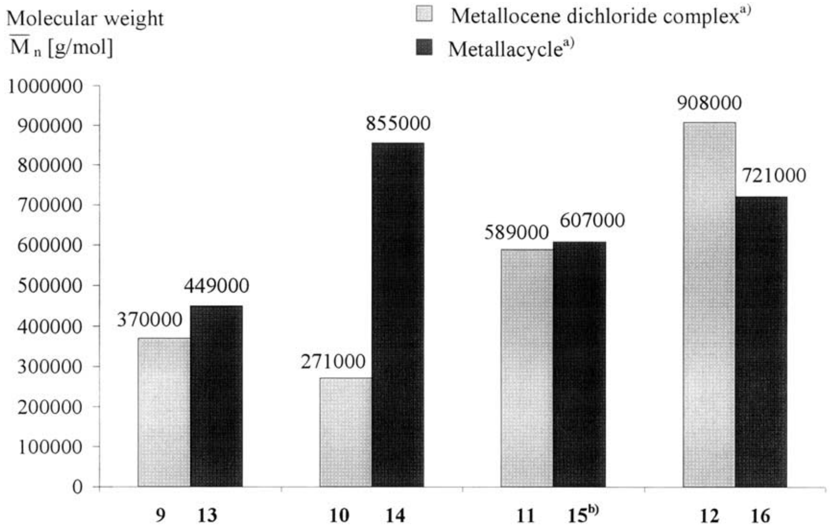


Fig. 9. Comparison of the molecular weights of polyethylenes prepared with the metallocene complexes **9**–**12** with mixed substituents and the corresponding metallacycles **13**–**16**. [a] Homogeneous polymerization in *n*-pentane at 60 °C (1 h) after activation with MAO (Zr–Al = 1:3000); [b] product mixture from **15A** and **15B**.

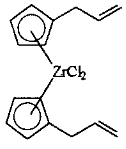
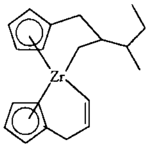
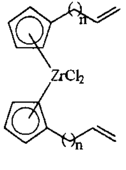
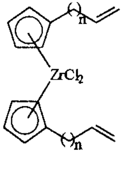
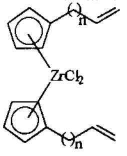
3.7. Activation of metallocene complexes with methylaluminoxane

5–10 mg of the corresponding metallocene complex was activated with MAO (30% in toluene) (Zr–Al = 1:3000). A quantity of catalyst solution corresponding to 0.2–1.0 mg of metallocene complex was used within 1 h for the homopolymerization.

3.8. Homopolymerization of ethylene

A 1 l Büchi laboratory autoclave was charged with 500 ml of *n*-pentane, the catalyst solution was added and the autoclave temperature was regulated to 60 °C. After the inside temperature had reached 50 °C an ethylene pressure (99.98% ethylene) of 10 bar was applied, the slurry was stirred for 1 h at 60 °C (±2) and

Table 2
^{1}H^a and ^{13}C-NMR^b data of metallocene complexes **1**–**16** (**1**, **3**–**5** and **9**–**12** measured in chloroform-d_1; **2**, **6**–**8** and **13**–**16** in benzene-d_6)

	^{1}H NMR$^{a)}$ [J(H,H) in Hz]	^{13}C NMR$^{b)}$
 **1**	6.32 (m, 4H), 6.21 (m, 4H), 5.89 (m, 2H), 5.07 (m, 4H), 3.41 (d, 4H) [6.5]	(C_q): 132.4 (CH): 116.9, 112.9 (CH_2): 116.8, 34.6
 **2**	7.39 (m, 1H), 7.02 (m, 1H), 6.44 (m, 1H), 6.17 (m, 1H), 5.69 (m, 1H), 5.67 (m, 1H), 5.41 (m, 1H), 5.11(m, 1H), 5.09 (m, 1H), 5.01 (m, 1H), 3.35 (m, 1H), 3.15 (m, 1H), 2.75 (m, 1H), 2.43 (m, 1H), 2.25 (m, 1H), 1.75 (m, 1H),1.33 (m, 1H), 1.14 (m, 1H), 0.98 (m, 1H), 0.86 (t, 3H) [6.9], 0.78 (d, 3H) [6.4], -1.36 (m, 1H)	(C_q): 142.0, 138.7 (CH): 183.3, 163.3, 117.1, 114.2, 108.2, 107.0, 105.9, 104.4, 103.4, 103.1, 57.6, 42.0 (CH_2): 61.2, 37.4, 33.3, 27.5 (CH_3): 15.7, 12.6
 **3** (n = 2)	6.16 (m, 4H), 6.07 (m, 4H), 5.66 (m, 2H), 4.85 (m, 4H), 2.60 (t, 4H) [6.5], 2.18 (m, 4H)	(C_q): 134.0 (CH): 137.4, 116.8, 112.1 (CH_2): 115.4, 34.5, 29.4
 **4** (n = 3)	6.28 (m, 4H), 6.19 (m, 4H), 5.78 (m, 2H), 4.99 (m, 4H), 2.63 (d, 4H) [7.6], 2.06, (m, 4H), 1.64 (m, 4H)	(C_q): 134.7 (CH): 138.2, 116.8, 112.2 (CH_2): 115.0, 33.3, 29.8, 29.5
	6.13 (m, 4H), 6.05 (m, 4H), 5.62 (m, 2H), 4.81 (m, 4H), 2.48 (d, 4H) [7.0], 1.93, (m, 4H), 1.42 (m, 4H), 1.30 (m, 4H)	(C_q): 134.5 (CH): 138.6, 116.6, 112.2 (CH_2): 114.4, 33.4, 30.0, 29.9, 28.4

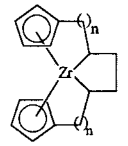
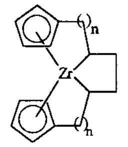
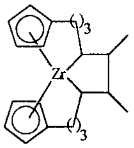
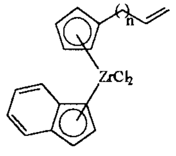
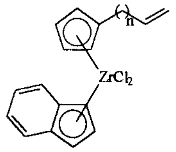
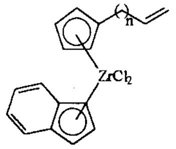
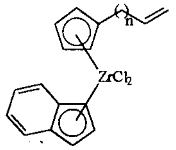
the reaction then terminated by releasing the pressure in the reactor. The polymer obtained was dried in vacuo.

3.9. Characterization of polyethylene samples

3.9.1. Differential scanning calorimetry (DSC)

The polymer samples were investigated for phase transitions by the DSC method with a Pyris DSC 7 instrument. For the test, 5–12 mg of dried polymer was sealed into standard aluminum dishes (∅ 7 mm) and measured under nitrogen cooling with the following temperature program: (1) Heating phase from 25 to 200 °C (heating rate 40 K min^{-1}), isothermal phase (3 min), cooling phase from 200 to −40 °C (cooling rate 20 K min^{-1}). (2) Heating phase from −40 to 200 °C (heating rate 20 K min^{-1}). The melting points and the enthalpies of fusion were measured during the second heating phase. The temperature was corrected linearly relative to indium (m.p.: 429.78 K); the enthalpy of fusion of indium ($H_m = 28.45$ J g^{-1}) was used for calibration.

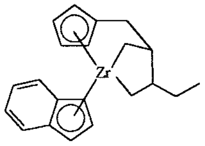
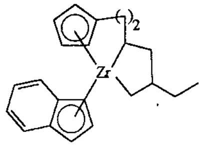
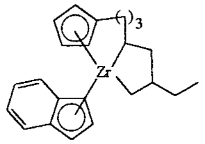
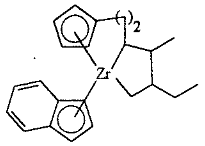
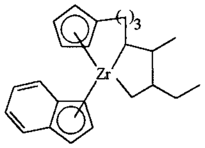
Table 2 (*Continued*)

5 (n = 4)		
 **6** (n = 2)	7.12 (m, 2H), 5.40 (m, 2H), 5.28 (m, 2H), 5.22 (m, 2H), 3.05 (m, 2H), 2.78 (m, 2H), 2.65 (m, 2H), 2,22 (m, 2H), 1.98 (m, 2H), 1.91 (m, 4H)	(C_q): 143.6 (CH): 118.1, 105.9, 103.9, 103.5, 59.5 (CH_2): 45.3, 27.0, 24.5
 **7** (n = 3)	6.51 (m, 2H), 5.91 (m, 2H), 5.00 (m, 2H), 4.75 (m, 2H), 2.88 (m, 4H), 2.2 – 0.86 (m, 14H)	(C_q): 143.3 (CH): 111.7, 111.3, 105.0, 102.3, 52.5 (CH_2): 35.8, 29.8, 29.2, 26.2
 **8** (n = 4)	6.65 (m, 2H), 5.81 (m, 2H), 5.07 (m, 2H), 4.81 (m, 2H), 2.77 (m, 2H), 2.2.2 (m, 2H), 2.05 – 0.82 (m, 18H)	(C_q): 143.7 (CH): 113.6, 113.5, 105.6, 103.8, 60.9, 42.5, (CH_2): 31.5, 29.8, 26.5 (CH_3): 19.6
 **9** (n = 1)	7.60 (m, 2H), 7.21 (m, 2H), 6.83 (t, 1H) [3.4], 6.44 (d, 2H) [3.4], 5.91-5.69 (m, 5H), 4.95 (m, 2H), 3.22 (d, 2H) [6.6]	(C_q): 139.9, 133.0 (CH): 135.8, 126.1, 125.4, 124.0, 117.1, 113.9, 112.5, 102.7 CH_2): 116.6, 34.2
 **10** (n = 2)	7.58 (m, 2H), 7.18 (m, 2H), 6.82 (t, 1H) [3.4], 6.42 (d, 2H) [3.4], 5.88 (m, 2H), 5.77 (m, 2H), 5.64 (m, 1H), 4.84 (m, 2H), 2.53 (t, 2H) [8.1], 2.13 (q, 2H) [8.1]	(C_q): 141.0, 134.6 (CH): 137.4, 126.1, 125.4, 124.0, 117.4, 113.5, 102.7 (CH_2): 115.4, 34.3, 29.3
 **11** (n = 3)	7.58 (m, 2H), 7.18 (m, 2H), 6.81 (t, 1H) [3.4], 6.42 (d, 2H) [3.4], 5.87 (m, 2H), 5.77 (m, 2H), 5.64 (m, 1H), 4.86 (m, 2H), 2.43 (t, 2H) [8.7], 1.92 (q, 2H) [8.7], 1.47 (qi, 2H) [8.7]	(C_q): 141.8, 135.2 (CH): 138.0, 126.0, 125.4, 123.9, 117.3, 113.6, 102.6 (CH_2): 114.9, 33.1, 29.4, 29.3
 **12** (n = 4)	7.54 (m, 2H), 7.16 (m, 2H), 6.80 (t, 1H) [3.4], 6.38 (d, 2H) [3.4], 5.82 (m, 2H), 5.23 (m, 2H), 5.59 (m, 1H), 4.83 (m, 2H), 2.39 (t, 2H) [8.7],	(C_q): 142.3, 135.3 (CH): 138.2, 126.0, 125.4, 124.0, 117.3, 113.6, 102.6 (CH_2): 114.5, 33.3, 29.8, 28.4

3.9.2. High temperature gel permeation chromatography (HT-GPC)

The polymers were analyzed with a HT-GPC 150C instrument from Millipore Waters Company. Four in-line columns filled with cross-linked polystyrene were used for separation. Pore diameters of the individual columns were 500, 1000, 10 000 and 100 000 Å. Detection was achieved by refractometry using a RI Waters 401 refractometer. Degassed 1,2,4-trichlorobenzene was used as eluent (flow rate 1 ml min^{-1}). The polymer samples were dissolved in boiling 1,2,4-trichlorobenzene and the measurements performed at 150 °C. The system was calibrated with a polystyrene standard.

Table 2 (*Continued*)

	1.91 (q, 2H) [8.7], 1.50-1.19 (m, 4H)	
 **13** (n = 1)	7.46 (m, 1H), 7.30 (m, 1H), 6.96 (m, 2H), 6.18 (m, 1H), 5.82 (m, 1H), 5.70 (m, 2H), 5.12 (m, 1H), 5.09 (m, 1H), 5.02 (m, 1H), 2.76 (m, 1H), 1.57-0.78 (m, 10H), 0.02 (m, 1H), -0.42 (m, 1H)	(C_q): 141.0, 133.5 (CH): 124.4, 124.0, 123.6, 123.3, 122.7, 114.4, 112.3, 110.8,105.0, 103.1, 97.6, 94.9, 49.1, 45.7 (CH_2): 54.6, 54.0, 38.3, 34.1 (CH_3): 11.6
 **14** (n = 2)	7.14 (m, 1H), 7.04 (m, 1H), 6.89 (m, 2H), 6.25 (m, 1H), 6.04 (m, 2H), 5.85 (m, 1H), 5.22 (m, 1H), 5.07 (m, 1H), 4.62 (m, 1H), 2.41 (m, 1H), 1.57-0.78 (m, 13H), 0.00 (m, 1H)	(C_q): 142.2 (CH): 124.6, 124.4, 123.7, 123.5, 119.2, 115.4, 107.2, 106.5, 105.2, 99.7, 97.4, 67.7, 38.8 (CH_2): 48.0, 46.1, 37.1, 36.6, 26.9 (CH_3): 11.9
 **15 A** (n = 3)	7.35-6.77 (m, 4H), 6.27 (m, 1H), 6.00 (t, 1H) [3.3], 5.81 (m, 1H), 5.74 (m, 1H), 5.14 (m, 1H), 4.88 (m, 1H), 4.57 (m, 1H), 2.70 (m, 1H), 1.82-0.73 (m, 15H), 0.16 (m, 1H)	(C_q): 142.4 (CH): 124.7, 124.4, 123.7, 123.6, 114.8, 112.3, 111.2, 106.0, 104.7, 101.0, 97.3, 60.9, 41.1 (CH_2): 46.6, 38.8, 37.6, 36.5, 28.7, 26.0 (CH_3): 11.8
 **15 B** (n = 3)	7.35-6.77 (m, 6H), 6.21 (m, 1H), 6.02 (t, 1H) [3.3], 5.87 (m, 1H), 5.13 (m, 1H), 4.56 (m, 1H), 2.34 (m, 1H), 1.82-0.73 (m, 15H), -0.29 (m, 1H)	(C_q): 142.4 (CH): 124.7, 124.4, 123.7, 123.6, 119.5, 115.9, 107.1, 106.1, 99.1, 98.2, 74.4, 47.6, 39.6 (CH_2): 50.3, 42.1, 30.6, , 26.5 (CH_3): 18.8, 10.7
 **16** (n = 4)	7.37 (m, 1H), 7.18 (m, 1H), 6.95 (m, 2H), 6.58 (m, 1H), 6.17 (m, 1H), 6.01 (t, 1H) [3.3], 5.91 (m, 1H), 5.81 (m, 1H), 4.86 (m, 1H), 4.61 (m, 1H), 2.76 (m, 1H), 1.83-0.78 (m, 16H), 0.61 (m, 1H), -0.13 (m, 1H)	(C_q): 141.1, 129.3 (CH): 124.9, 124.8, 124.2, 124.0, 116.5, 114.1, 113.1, 107.1, 106.1, 100.8, 99.0, 67.5, 50.5, 43.6 (CH_2): 52.7, 32.4, 31.0, 29.7, 26.8 (CH_3): 19.7, 11.0

a) 25 °C, in chloroform–d_1 δ [ppm] rel. chloroform (7.15).
25 °C, in benzene-d_6 δ [ppm] rel. benzene (7.24).

b) 25 °C, in chloroform –d_1 δ [ppm] rel. chloroform –d_1 (77.0).
25 °C, in benzene -d_6 δ [ppm] rel. benzene -d_6 (128.0).

Table 3
MS data of compounds **1** and **3**–**5**

Compound	M^+ [*m*/*e*]
1	372
3	401
4	429
5	457

Table 4
MS data of compounds **9**–**12**

Compound	M^+ [*m*/*e*]
9	382
10	396
11	410
12	424

Acknowledgements

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