Journal of Molecular Catalysis A: Chemical 165 (2001) 23–32

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Heterogeneous metallocene catalysts for ethylene polymerization

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Received 18 May 2000; accepted 11 September 2000

Dedicated to Professor Dr. Henri Brunner on the occasion of his 65th birthday (4 October 2000)

Abstract

The catalyst precursor 9-fluorenylidene-1-cyclopentadienylidene-2-hex-5-enylidene zirconium dichloride proved to be highly active in the heterogeneously catalyzed polymerization of ethylene using silica gel/partially hydrolyzed trimethylaluminum (PHT) as cocatalyst. The substitution of position 4 of the fluorenylidene fragment and position 3 of the cyclopentadienylidene ring improves the catalyst activity. The introduction of a phenyl group into the bridge increases the catalyst activity and the molecular weight of the polymer. The prepolymerization of this catalyst system leads to a major change in catalyst and polymer properties. A significant increase in catalyst activity and a lower molecular weight of the produced polyethylene is observed. The presence of hydrogen during prepolymerization or polymerization of ethylene produces a broader molecular weight distribution indicating a higher number of different active centers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ethylene polymerization; Metallocene catalysts; PHT; High activity

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1. Introduction

Until now, *ansa*-fluorenylidene cyclopentadienylidene zirconium dichloride complexes [1–6], activated with MAO, found only limited application in ethylene polymerization. The activity of ($C_{13}H_8$–CMe_2–C_5H_4)$ZrCl_2$/MAO for instance is lower by a factor of 30 than the activity achieved with $(C_5H_5)_2ZrCl_2$/MAO. Although, at an extreme excess of MAO (Al:Zr = 10,000:1) [7] catalyst activities can go up to 60,000 kg PE/g Zr h. This is 10–100 times higher than for conventional Ziegler–Natta catalysts. Commercial applications of these homogeneous metallocene catalysts remain unattractive due to their high fouling potential and the expense associated with the use of large amounts of MAO. Immobilization of these homogeneous catalysts normally leads to drastic activity decreases during ethylene polymerization. Here we report a method of converting various homogeneous *ansa*-fluorenylidene cyclopentadienylidene zirconium dichloride complexes, activated with MAO, into heterogeneous catalysts by use of silica gel/PHT [8] as cocatalyst. In addition, very low aluminum/zirconium ratios yield much higher activities for ethylene polymerization than do the corresponding homogeneous catalysts activated with MAO. The influence of hydrogen and the application of a prepolymerization step were also investigated.

2. Results and discussion

Specific metallocene dichloride complexes with olefinic substituents [9,10] have proven to be highly active catalysts after activation with silica gel/PHT [8]. The polymerization experiments in this study were performed using C_1-bridged fluorenylidene cyclo-

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PII: S1381-1169(00)00421-0

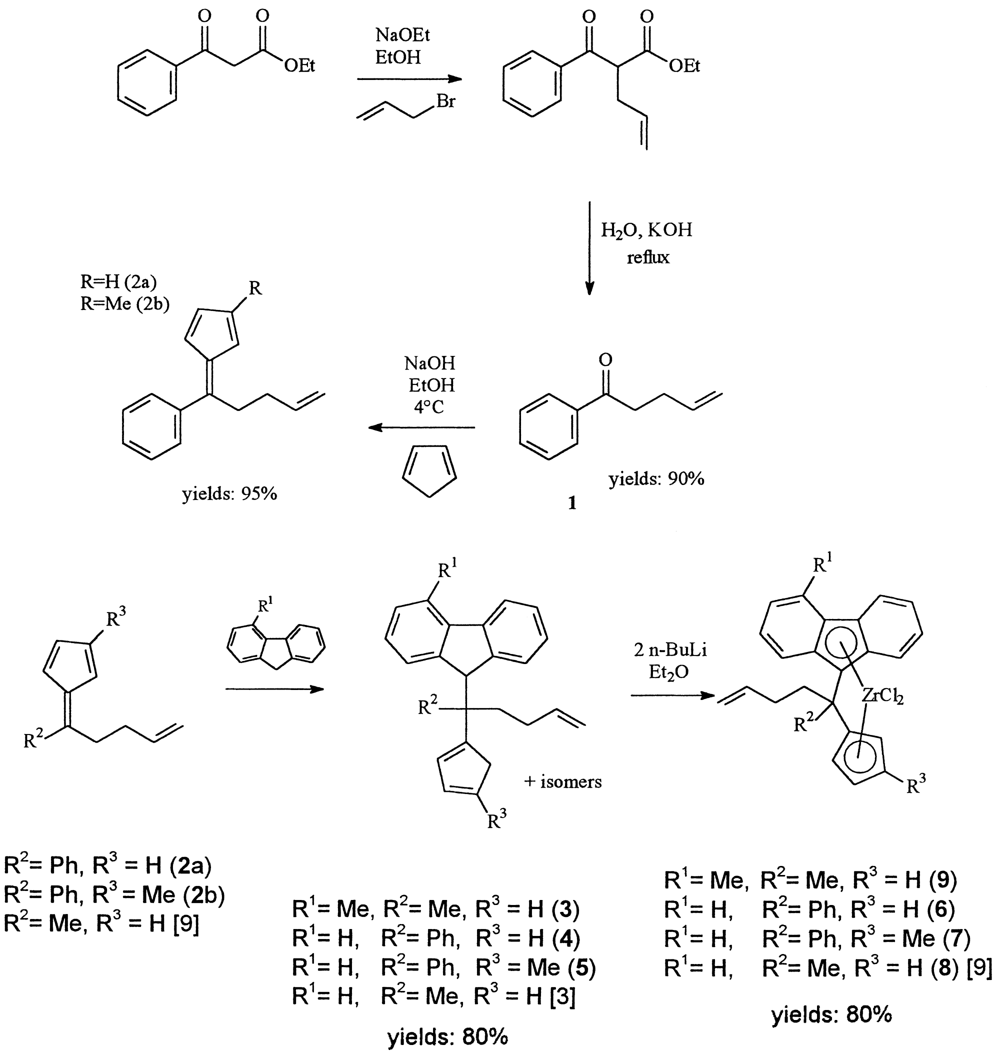
pentadienylidene zirconium dichloride complexes because these catalyst precursors can easily be synthesized.

2.1. Synthesis of the metallocene dichloride complexes

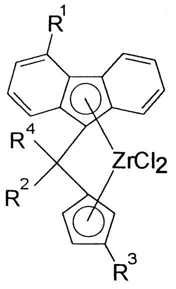
The synthesis of the catalyst precursors is analogous to the synthesis of 9-fluorenylidene-(1-phenyl-1-pent-5-enylidene)-1-cyclopentadienylidene zirconium dichloride presented as example in Scheme 1. The ligand and catalyst precursors (Scheme 2) were characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 1) as well as mass spectroscopy.

2.2. Prepolymerization experiments

Various patents on the heterogeneous, metallocene catalyzed olefin polymerization describe the prepolymerization of the activated catalyst suspension with ethylene [11,12]. The pre-polymerization is performed to achieve uniform catalyst particle size and, as a con-



Scheme 1. Syntheses of **1**–**9**.



Number	R^1	R^2	R^3	R^4
6	H	Ph	H	$^{=}C_4$
7	H	Ph	Me	$^{=}C_4$
8 [9]	H	Me	H	$^{=}C_4$
9	Me	Me	H	$^{=}C_4$
10	H	Me	H	C_4

Notes to Scheme 2: $^{=}C_4$ = ω-butenyl, C_4 = n-butyl.

Scheme 2. Summary of the prepared metallocene dichloride complexes **6**–**10**.

sequence, uniform polymer particle size without the presence of very fine polymer particles. Major changes in catalytic or polymer properties are not described.

The influence of a prepolymerization step was investigated using the silica gel/PHT system with two catalyst precursors: (9-fluorenylidene-1-cyclopentadienylidene)-2-hex-5-enylidene zirconium dichloride (**8**) [9] and (9-fluorenylidene-1-cyclopentadienylidene)-2-hexylidene zirconium dichloride (**10**). In addition, the influence of hydrogen on catalytic and polymer properties was investigated. Therefore, the experiments listed in Scheme 3 were conducted. The prepolymerization of SiO_2/PHT/**8** was performed without hydrogen (**15**) and in the presence of hydrogen (**16**). Two polymerizations of ethylene with SiO_2/PHT/**8** with (**14**) and without hydrogen (**13**) were also performed.

2.3. *Polymerization experiments*

The above synthesized metallocene dichloride complexes were used in combination with the cocatalyst for heterogeneous ethylene polymerization as indicated in Table 2. The catalytic and polymer analytic results are summarized in Table 2.

2.3.1. *Influence of the catalyst precursor*

The influence of the substituents on the polymerization behavior and the polymer properties was investigated with the highly active catalyst precursor (9-fluorenylidene-1-cyclopentadienylidene)-2-hex-5-enylidene zirconium dichloride (**8**) and various, selected derivatives. Silica gel/PHT was used as cocatalyst with an aluminum/zirconium ratio of 260:1.

The activity of silica gel/PHT/**8** (**13**) is 518 kg PE/g Zr h. Therefore, this precursor exhibits a significantly higher catalytic potential than its saturated analogue silica gel/PHT/**10** (**18**). Obviously, the unsaturated group in the bridge of the ligand structure has an enormous influence on the activity of this compound. A striking difference in the catalytic potential is also observed when silica gel/PHT/**8** is compared with MAO/**8**. Despite the lower Al/Zr ratio (factor 10), silica gel/PHT/**8** exhibits a six times higher activity in ethylene polymerization. The molecular weight of the polymer also increases by a factor of three (350 kg/mol).

Methyl substituents on the fluorenylidene (silica gel/PHT/**9**) as well as on the cyclopentadienylidene fragment (silica gel/PHT/**7**) also increase the activity. This observation supports previous hypotheses about the effect and structure of methylaluminoxane [13]. Substitution in position 4 of the fluorenylidene, or position 3 of the cyclopentadienylidene fragment obviously increases the distance between the metallocene monoalkyl cation and the complex MAO anion. Since the catalytic activity of the cationic metallocene fragment is increased by separation of the contact ion pair [14–17], complexes with corresponding substituents are excellent catalyst systems [13].

The substitution of one methyl group on the bridging carbon by one phenyl group also has a significant impact on the catalytic and polymer properties. As expected, the molecular weight of the polymer obtained with silica gel/PHT/**6** [18] increases ∼50% compared to the polymer obtained from silica gel/PHT/**8**. Surprisingly, a large activity was also observed. This activity increase as well as the increased molecular weight of the polymer suggest that the phenyl group has an electronic influence on the active metallocene cation. In this case, steric reasons do barely play a role because the phenyl group is not located in the

Table 1
^{1}H and ^{13}C NMR spectroscopic data of compounds **1**–**7** and **9**

No.	^{1}H NMR[a]	^{13}C NMR[b]
1	7.87 (m, 2H), 7.43–7.31 (m, 3H), 5.91–5.75 (m, 1H), 5.04–4.90 (m, 2H), 2.95 (m, 2H), 2.41 (m, 2H)	199.1 (C_q), 136.7 (C_q), 133.5 (CH), 129.3 (CH), 128.4 (CH), 115.1 (CH_2), 37.5 (CH_2), 28.0 (CH_2)
2a	7.53 (m, 5H), 6.83–6.33 (m, 3H), 6.34 (d, 1H), 6.11–5.92 (m, 1H), 5.22–5.11 (m, 2H), 3.20 (m, 2H), 2.39 (m, 2H)	152.9 (C_q), 143.6 (C_q), 140.4 (C_q), 137.1 (CH), 131.9 (CH), 131.5 (CH), 129.4 (CH), 128.0 (CH), 127.9 (CH), 123.7 (CH), 120.8 (CH), 115.1 (CH_2), 35.4 (CH_2), 33.5 (CH_2)
2b	7.46 (m, 5H), 6.89–6.20 (2H), 5.93 (m, 2H), 5.13 (m, 2H), 3.11 (m, 2H), 2.35–2.16 (m, 5H)	149.2 (C_q), 144.0 (C_q), 143.8 (C_q), 143.4 (C_q), 140.8 (C_q), 137.3 (CH), 137.2 (CH), 134.7 (CH), 134.3 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.3 (CH), 127.9 (CH), 127.6 (CH), 124.6 (CH), 121.6 (CH), 119.0 (CH), 116.4 (CH), 114.5 (CH_2), 35.2 (CH_2), 35.0 (CH_2), 33.4 (CH_2), 33.3 (CH_2), 15.5 (CH_3), 15.3 (CH_3)
3	7.96 (d, 1H), 7.57 (d, 1H), 7.44–7.10 (m, 5H), 6.71–6.52 (m, 3H), 5.92 (m, 1H), 5.14 (m, 2H), 3.14 (m, 2H), 2.79 (s, 3H), 2.22–1.89 (m, 4H), 0.86 (s, 3H)	Not determined
4	7.78 (m, 2H), 7.63 (m, 1H), 7.29–7.01 (m, 10H), 6.40 (m, 1H), 6.32 (m, 1H), 6.21 (m, 1H), 6.11 (m, 1H), 5.96 (m, 2H), 5.06 (m, 2H), 4.23 (s, 1H), 4.19 (s, 1H), 3.05–3.00 (m, 2H), 2.10 (m, 4H)	154.6 (C_q), 152.3 (C_q), 145.1 (C_q), 144.7 (C_q), 142.4 (C_q), 141.0 (C_q), 139.6 (CH), 139.4 (CH), 139.1 (CH), 135.4 (CH), 129.3 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 126.5 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 125.6 (CH), 125.2 (CH), 119.5 (CH), 119.1 (CH), 113.2 (CH_2), 55 (CH), 54.7 (CH), 43.3 (CH_2), 43.1 (CH_2), 37.7 (CH_2), 29.9 (CH_2), 29.7 (CH_2)
5	7.61–7.13 (m, 3H), 7.25–6.95 (m, 10H), 5.95–5.63 (m, 2H), 5.00–4.76 (m, 3H), 2.78–2.24 (m, 4H), 1.93–1.60 (5H)	148.0 (C_q), 145.1 (C_q), 142.9 (C_q), 141.8 (C_q), 138.7 (CH), 129.3 (CH), 128.3 (CH), 128.1 (CH), 127.0 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 126.2 (CH), 126.0 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH), 118.9 (CH), 118.7 (CH), 118.6 (CH), 113.6 (CH_2), 55.0 (CH), 54.6 (CH), 52.2 (CH), 43.3 (CH_2), 37.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 15.4 (CH_3)
6	7.82 (m, 2H), 7.62 (m, 1H), 7.49 (m, 2H), 7.42–7.10 (m, 7H), 6.72 (m, 1H), 6.15 (m, 2H), 5.76 (m, 1H), 5.52 (m, 2H), 5.02 (m, 2H), 2.89 (m, 1H), 2.71 (m, 1H), 2.14 (m, 2H)	142.2 (C_q), 137.2 (CH), 135.2 (C_q), 132.0 (C_q), 129.8 (CH), 129.2 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.4 (CH), 127.1 (CH), 127.0 (CH), 126.8 (CH), 126.7 (CH), 124.8 (CH), 124.7 (CH), 124.2 (CH), 123.5 (CH), 122.7 (CH), 119.7 (CH), 114.7 (CH_2), 103.0 (CH), 102.4 (CH), 39.2 (CH_2), 28.2 (CH_2)
7	8.21 (m, 2H), 7.80 (m, 2H), 7.61–7.29 (m, 8H), 6.89 (m, 1H), 6.2–5.5 (m, 4H), 5.42–5.09 (m, 2H), 3.07 (m, 1H), 2.82 (m, 1H), 2.34–1.93 (m, 5H)	142.1 (C_q), 137.5 (CH), 131.8 (C_q), 129.8 (C_q), 129.7 (CH), 129.6 (CH), 128.6 (CH), 128.5 (CH), 127.5 (CH), 127.4 (CH), 127.1 (CH), 125.1 (CH), 125.0 (CH), 124.3 (CH), 124.3 (C_q), 123.2 (C_q), 118.9 (CH_2), 111.5 (C_q), 105.1 (CH), 104.9 (CH), 104.4 (CH), 103.7 (CH), 53.5 (C_q), 39.6 (CH_2), 39.5 (CH_2), 28.4 (CH_2), 15.2 (CH_3)
9	8.13 (m, 2H), 7.81 (m, 1H), 7.59 (m, 3H), 7.27 (m, 2H), 6.35 (m, 2H), 6.00 (m, 1H), 5.76 (m, 2H), 5.14 (m, 2H), 3.34 (m, 1H), 2.57 (m, 2H), 2.42 (s, 3H), 2.22 (m, 1H)	137.6 (C_q), 129.5 (C_q), 129.7 (CH), 125.3 (CH), 125.1 (CH), 124.8 (CH), 123.5 (CH), 123.1 (CH), 123.0 (C_q), 122.1 (C_q), 119.9, 119.0, 114.9 (CH_2), 114.7 (C_q), 102.5 (CH), 101.9 (CH), 78.4 (C_q), 45.2 (C_q), 40.0 (CH_2), 27.3 (CH_2), 25.9 (CH_3), 22.0 (CH_3)

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

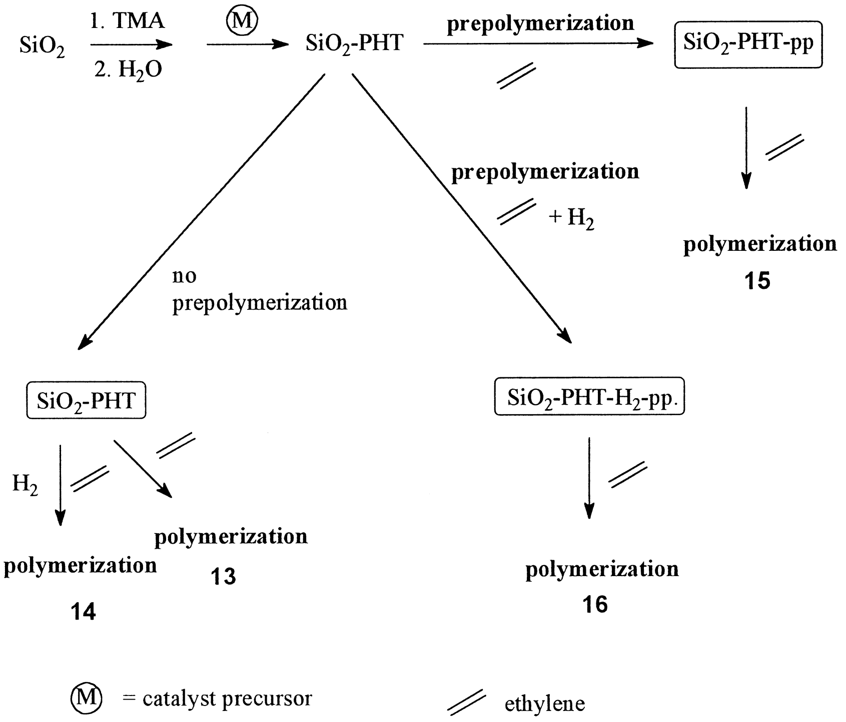
[b] 25°C, in chloroform-d_1, δ (ppm) rel. chloroform-d_1 (77.0).

spatial proximity of the coordination sphere of the monomer.

2.3.2. *Influence of prepolymerization*

The influence of prepolymerization was investigated using the silica gel/PHT system with the two catalyst precursors **8** and **10**. Due to prepolymerization, the activity of the catalyst increases and simultaneously the molecular weight of the produced polymer decreases for catalysts **15** and **19**.

The polyethylene produced with SiO_2/PHT/**8** (**13**) exhibits a molecular weight distribution of $M_w/M_n \approx$



Scheme 3. Polymerization and prepolymerization experiments with catalyst precursor **8**.

4. This is a broader molecular weight distribution than expected for most metallocene catalysts ($M_w/M_n \approx < 3$). On closer examination of the GPC curve of **13** in Scheme 4, a shoulder can be recognized, indicating a deviation from the ideal Schulz–Flory distribution [19]. Thus, catalyst **13** contains at least two different active sites, each producing a polymer with different molecular weight. For the prepolymerized catalyst **15**,

Table 2
Polymerization results of the catalysts **11**–**20**

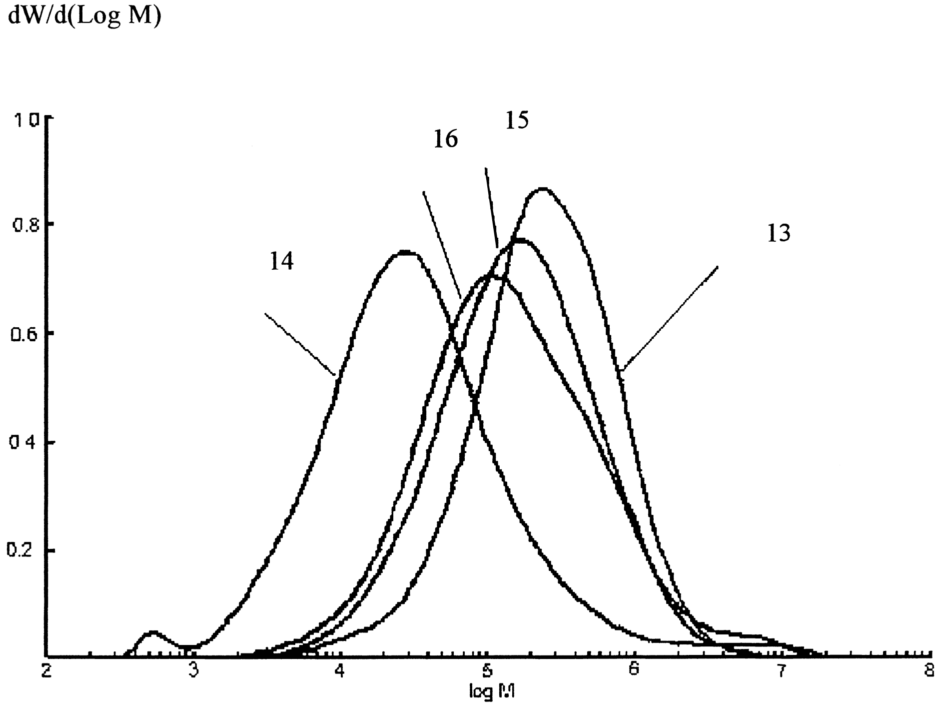
No.	Catalyst	Activity (kg PE/g Zr h)	$M_\eta/10^3$ (kg/mol)[a]	$M_w/10^3$ (kg/mol)[a]	$M_n/10^3$ (kg/mol)[a]	M_w/M_n	T_m (°C)	ΔH_m (J/g)	α (%)
11	SiO_2/PHT/**6**[b]	720	480[c]	–	–	–	140.2	150.2	51
12	SiO_2/PHT/**7**[b]	890	520[c]	–	–	–	138.6	144.2	49
20	MAO/**8**[b]	87	112[c]	–	–	–	137.5	113.6	39
13	SiO_2/PHT/**8**[b]	518	348	399	109	3.66	139.1	133.9	45
14	SiO_2/PHT/**8** + H_2[b]	240	74	117	11.3	10.4	136.6	165.7	57
15	SiO_2/PHT/**8**-pp.[d]	810	211	252	57.9	4.35	137.3	139.9	48
16	SiO_2/PHT/**8**-H_2-pp.[d]	670	296	396	57.2	6.93	136.7	154.5	53
17	SiO_2/PHT/**9**[b]	550	330[c]	–	–	–	134.7	134.1	46
18	SiO_2/PHT/**10**[d]	78	340[c]	–	–	–	–	–	–
19	SiO_2/PHT/**10**-pp.[d]	115	260[c]	–	–	–	–	–	–

[a] All molecular weights were determined using high temperature gel permeation chromatography and universal calibration.

[b] Polymerization conditions: 10.0 bar ethylene pressure; 500 ml *n*-pentane; 1.0 ml TIBA (1.6 M in *n*-hexane); 70°C; heterogeneous reaction course; Al:Zr = 260:1; Al:O = 1.44:1; carrier portion of the catalyst: 36%.

[c] Molecular weight determined using capillary viscosimetry.

[d] As in footnote b, except: catalyst suspension in toluene 15 min prepolymerized; carrier SiO_2; portion of the catalyst: 34%.



Scheme 4. Gel permeation chromatograms of the polyethylenes produced with **13**–**16**.

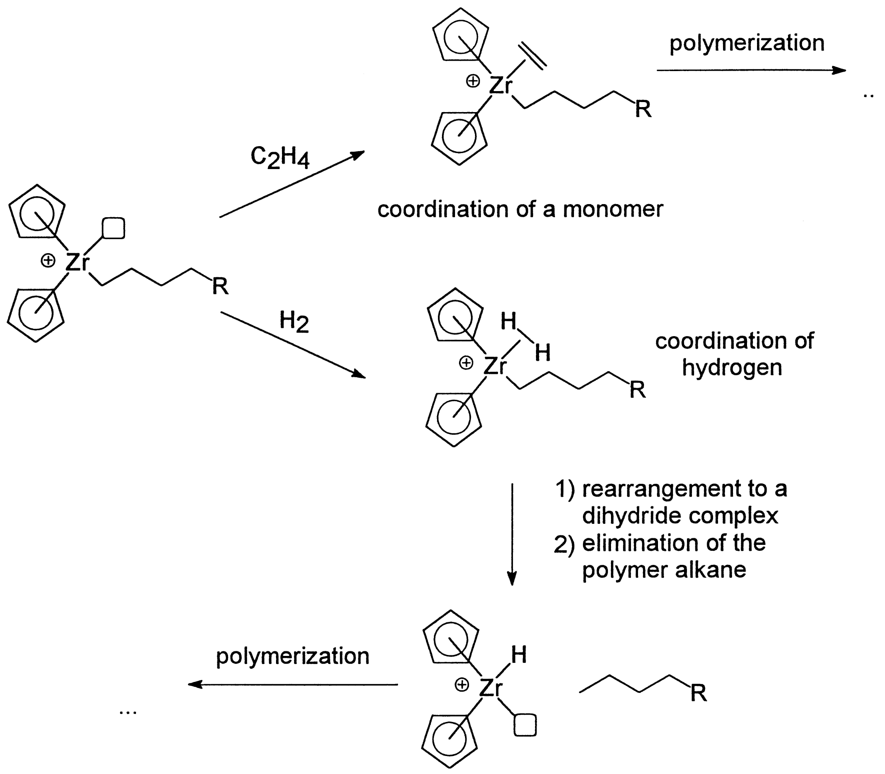
M_w as well as M_n decrease and simultaneously the polydispersity (M_w/M_n) increases by 0.7–4.35. Presumably, the activity increasing effect results from the avoidance of the first growth step, the insertion of ethylene into the zirconium–methyl bond. Kinetic studies reveal that for almost all non-prepolymerized PHT systems there is an induction phase of approximately 8 min, and, only after the induction period, there is an increase in the production rate. This induction phase is limited to a maximum of 2 min for the prepolymerized catalysts **15** and **19**.

2.3.3. *Influence of hydrogen*

Metallocene catalysts can polymerize olefins to give polymers with narrow molecular weight distributions ($M_w/M_n \approx 2$) and high molecular weights ($5\times10^4 < M_w < 2\times10^6$) [15,16,20]. However, these polymers exhibit adverse processing characteristics so that industrial applications are very limited. Hydrogen is added to the polymerization reaction to obtain polymers with lower molecular weights for better processing [20–22]. In contrast to most Ziegler–Natta heterogeneous catalysts, only traces of hydrogen are sufficient to change the molecular weight over a large range in metallocene catalyzed polymerizations. Hydrogen must compete effectively with the monomer for the catalyst center (Scheme 5).

Analogous like an olefin, also a hydrogen molecule can be bonded to the free coordination site on the metal center. A polymer chain with a saturated end group is eliminated due to hydrogen insertion into the metal–carbon bond. The formed hydride species, similar to the analogous alkyl species, is an effective catalysis center, i.e. the metallocene catalyst is not deactivated by hydrogen. Only the use of high hydrogen concentrations increasingly blocks the coordination of an ethylene molecule, leading to activity losses.

The results from Table 2 make it obvious that the catalyst productivity tremendously decreases in the presence of hydrogen in the reactor (**13** and **14**). This could result from a competition reaction of hydrogen with the active metal centers, whereby ethylene molecules are inhibited in their coordination. Consequently, the growth rate of the polymer chain decreases. Simultaneously, the molecular weight M_w decreases significantly. The reason for this behavior



Scheme 5. Influence of hydrogen on ethylene polymerization.

could be the chain terminating effect of hydrogen. M_n decreases even more, resulting in a broader molecular weight distribution of $M_w/M_n = 10.4$. This broader molecular weight distribution (Scheme 4) results from the additional termination reaction induced by hydrogen.

A comparison of **15** and **16** again shows a decrease in catalyst productivity. The use of hydrogen during prepolymerization (**16**) increases the molecular weight M_w of the polymer by more than 50%. At constant M_n, a broader molecular weight distribution ($M_w/M_n = 6.93$) is obtained. The analysis of the gel permeation chromatogram of the polymer produced with **16** exhibits several "shoulders" in the curve. Consequently, the addition of hydrogen leads to various, active centers, i.e. a "dual-site" catalyst (**13**) with at least two catalyst centers ($M_w/M_n \approx 4$) is transformed into a "multi-site" catalyst (**16**) with several different active centers ($M_w/M_n \approx 7$). Since each catalyst species produces a different polymer when hydrogen is used during prepolymerization, a uniform molecular weight distribution is transformed into a multimodal distribution of the molecular weights for the synthesized polymers.

2.3.4. Polymerization of propylene

It was also of interest to test the heterogeneous catalyst system **13** for the produvtivity of syndiotactic polypropylene [9]. Likewise, SiO_2/PHT/*rac*-bis(2-methylindenylidene) dimethyl-silylidene zirconium dichloride [23] was tested for the production of isotactic propylene polymerization. In contrast to the activation of these catalysts with MAO [9,23], in homogeneous solution the employed catalysts proved to be completely inactive for bulk propylene polymerization at 70°C.

3. Experimental part

NMR spectroscopic investigations were routinely performed using the Bruker ARX 250 instrument. All organometallic samples were prepared under argon and measured at 25°C. $CDCl_3$ served as solvent. The chemical shifts (δ) in ^{1}H NMR spectroscopy are referred to the residual proton signal of the solvent $CHCl_3$ ($\delta = 7.24$ ppm) and in ^{13}C NMR spectroscopy to the solvent signal ($\delta = 77.0$ ppm for chloroform-d_1).

Thermal properties of the polymer samples were investigated for phase transitions using DSC. A NETZSCH DSC 200 instrument was available. For the measurements, 3–6 mg of the dried polymers were fused into standard aluminum pans (∅, 5 mm) and measured under nitrogen cooling using the following temperature program: First heating phase: from 60 to 200°C, heating rate 20 K/min, isothermal phase (3 min), cooling phase from 200 to 60°C, cooling rate 20 K/min. Second heating phase from 60 to 200°C, heating rate 20 K/min, isothermal phase (3 min), cooling phase from 200 to 20°C, cooling rate 20 K/min. Melting points and fusion enthalpies were derived from the 2 h heating course. The temperature was linearly corrected relative to indium (mp, 156.63°C). The fusion enthalpy of indium ($\Delta H_\mathrm{m} = 28.45$ J/g) was used for calibration.

The molecular weight determination of the polymer samples was performed using an Ubbelohde precision capillary viscometer in *cis*/*trans*-decalin at 135 ± 0.1°C. Therefore, the polymer samples were completely dissolved in decalin at 130°C over a period of 3–4 h. $\bar{M}_\eta$ was determined using calibration curves that were available for three different concentrations.

All the work was routinely carried out with Schlenk technique under strict exclusion of air and moisture. Purified and dried argon was used as inert gas.

3.1. Synthesis of 5-phenyl-pent-1-en-5-one (**1**)

33.0 g sodium were dissolved in 1000 ml ethanol. 260 ml benzoyl acetic ester were added to the still warm ethanolate solution, and then 130 ml 3-bromopropene (allyl bromide) were added dropwise to the solution. The mixture was heated for 4 h under reflux. After the solvent was evaporated, 145 g potassium hydroxide were dissolved in 500 ml water, added to the reaction mixture and heated for 4 h under reflux. After cooling the mixture to room temperature, it was neutralized with 0.5 M hydrochloric acid. The mixture was extracted three times with 150 ml diethylether each. The organic phases were separated, washed twice with water and dried. After the solvent was evaporated in vacuo, the product was obtained as light yellow liquid (yield: 90%). Electron impact ionization mass spectrometry (EI-MS): $m/e(I_\mathrm{rel}) = 160$ (**1**).

3.2. General synthesis procedure for the phenyl substituted fulvene derivatives **2*a*** and **2*b***

4.30 g sodium were dissolved in 150 ml ethanol, dried over molecular sieve. Subsequently, the solution was cooled to 0°C. After the addition of 30 g (0.19 mol) 5-phenyl-pent-1-en-5-one (**1**), 0.35 mol of the respective cyclopentadiene derivative were added slowly to the solution and stirred for 4 h at room temperature. 100 ml water and 100 ml *n*-pentane were added to the orange-red solution. The aqueous phase was extracted twice with 75 ml *n*-pentane, the organic phases were dried over sodium sulfate and filtered over silica gel. After the solvent was evaporated in vacuo, the fulvene remained as red oil. Yield: 85–95%. EI-MS: $m/e(I_\mathrm{rel}) = 208$ (**2a**), 222 (**2b**).

3.3. General synthesis procedure for the C_1-bridged ligand precursors **3**–**5**

0.06 mol of the corresponding fluorenyl derivative were dissolved in 250 ml ether and mixed with 37.5 ml (0.06 mol) *n*-butyllithium (1.6 M solution in *n*-hexane) at room temperature. The solution was stirred for 4 h at room temperature. Subsequently, one equivalent of the corresponding fulvene derivative was added at −78°C and stirred for 18 h at room temperature. The solution was stirred for 30 min after the addition of another 1.0 ml *n*-butyllithium, and 200 ml water were added. The organic phase was dried over sodium sulfate and the solvent was evaporated in vacuo. The residue was dissolved in *n*-pentane, the solution was filtered over silica gel and the solvent evaporated. The ligand precursors were crystallized from *n*-pentane at −25°C. Yields: 70–85%; colorless crystals. EI-MS: $m/e(I_\mathrm{rel}) = 326$ (**3**), 374 (**4**), 388 (**5**).

3.4. General synthesis procedure for the metallocene dichloride complexes **6**, **7**, **9**

The appropriate ligand precursor, 0.01 mol, was dissolved in 200 ml diethylether and mixed with

0.02 mol *n*-butyllithium (1.6 M solution in *n*-hexane) at −78°C. After warming up to room temperature, the mixture was stirred for 4 h. Subsequently, at −78°C, 2.33 g (0.01 mol) zirconium tetrachloride were added and stirred for 12 h at room temperature. Then, the solvent was evaporated and the residue was extracted with dichloromethane and the solution was filtered over sodium sulfate. The solution was reduced in volume and crystallized at −78°C. The metallocene dichloride complexes were obtained in yields between 60 and 80%. EI-MS: $m/e(I_{\mathrm{rel}}) = 534$ (**6**), 548 (**7**), 486 (**9**).

3.5. General synthesis procedure for the silica gel/PHT catalyst system

At room temperature, 30 ml of a 2.0 M trimethylaluminum solution in toluene were added to a suspension of 2.0 g calcined silica gel in 100 ml toluene. 0.75 ml water was bubbled through the suspension as a moist argon flow. Thereupon, the reaction mixture heated itself to 60°C. After 10 min, the suspension became suddenly highly viscous. After cooling to room temperature, the mixture was stirred vigorously for 2 h. Finally, 0.23 mmol of the catalyst precursor were added as solids and stirred for 5 min. Finally, the mixture was filtered and the solution dried in vacuo. The filtrate was colorless and contained no organic or inorganic components besides the solvent. Yields of the catalyst: 5.40 g (>95% calculated on aluminum content) of a powder colored according to the catalyst precursor.

3.6. General synthesis procedure for the prepolymerized silica gel/PHT catalyst system

The synthesis follows analogous to 3.5. However, an ethylene pressure of 1.0 bar was applied for 15 min at 25°C prior to the filtration of the catalyst suspension. If a prepolymerization should be conducted in the presence of hydrogen, the reaction vessel was saturated with hydrogen at ambient pressure prior to the addition of ethylene. During prepolymerization, the color of the reaction mixture changed to dark-brown and it became highly viscous. After filtration and drying in vacuo, 5.60 g of a slightly colored powder were obtained. The polyethylene portion of the catalyst was obtained from the difference between the weight before and after prepolymerization.

3.7. Polymerization with silica gel/PHT

500 ml *n*-pentane with 1.0 ml trisobutylaluminum (1.6 M solution in *n*-hexane) was added to a 1 l round bottom flask and stirred for 10 min. The catalyst, 0.20 g, was added as powder to this solution. If the polymerization should be conducted in the presence of hydrogen, the reactor was filled with 300 ml hydrogen at ambient pressure. The suspension was subsequently transferred into a 1 l Büchi laboratory autoclave filled with argon or argon/hydrogen, heated to 70°C and an ethylene pressure of 10 bar was applied (99.98% ethylene, previously dried over aluminum oxide). The amount of ethylene that was consumed was registered with a Büchi-Press-Flow-Control BPC 9901. The mixture was stirred for 1 h and the reaction was terminated by releasing the pressure from the reactor. The obtained polymer was dried in vacuo until a constant weight was obtained.

Acknowledgements

We thank Phillips Petroleum Company, Bartlesville, OK, USA, for the financial support.

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