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Journal of Organometallic Chemistry 568 (1998) 263–269

Journal of Organo metallic Chemistry

Polymerization of ethylene with metallocene/methylaluminoxane catalysts supported on polysiloxane micro gels and silica

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Received 2 June 1998

Abstract

Two kinds of fluorenyl containing zirconocene catalysts, supported on polymethylsiloxane micro gels and on silica, were prepared and applied for ethylene polymerizations using methylaluminoxane as cocatalyst. The observed activities were comparable with those of the corresponding silica supported catalysts. The average molecular weights of the obtained polymers differ from those of the corresponding homogeneous catalysts as from those of the silica supported systems.

Keywords: Metallocene catalysts; Micro gels; Silica; Support; Ethylene polymerization

1. Introduction

Since the discovery of highly active metallocene catalysts by Kaminsky and Sinn [1] many efforts have been made to investigate catalyst systems based on Group 4 metallocene complexes [2–9]. In combination with methylaluminoxane (MAO) as cocatalyst or activated with non coordinating anions [10–12] these metallocene complexes allow unprecedented control on the polyolefin structure due to catalyst design. They also enable the synthesis of novel types of homo- and copolymers of α-olefins [13–15], cyclic olefins [16] and dienes [17]. Although these catalyst systems offer the capability for the synthesis of polymeric materials with unique properties, technical problems due to their homogeneous character are arising. Heterogenization of homogeneous catalysts avoids reactor fouling and provides products with larger, more uniform particle size and higher bulk density. Industrial scale production of polyolefins (e.g. in slurry or gas phase processes) is accomplished using heterogeneous catalysts. Another advantage of heterogenization is the facile control of the polymer particle morphology by using established technology for common Ziegler–Natta catalysts [18].

Recently, some reports have been published concerning supported metallocene catalysts for the polymerization of olefins [19–22]. To propose the properties of an entirely new supporting material with specific features we report on the synthesis of new heterogeneous metallocene catalysts immobilized on a polysiloxane micro gel [23,24]. Silica is a widely used support for the immobilization of homogeneous catalysts [25–29]. Therefore we compare the polyethylenes that had been obtained with the polysiloxane supported catalysts, with SiO_2 immobilized catalysts and in homogeneous solution.

2. Results and discussion

In this work we describe the first immobilization of metallocene catalyst precursors on polyorganosiloxane micro gels. The surface of these spherical, redisperible polysiloxanes can easily be tailored by the introduction of functionalized substituents.

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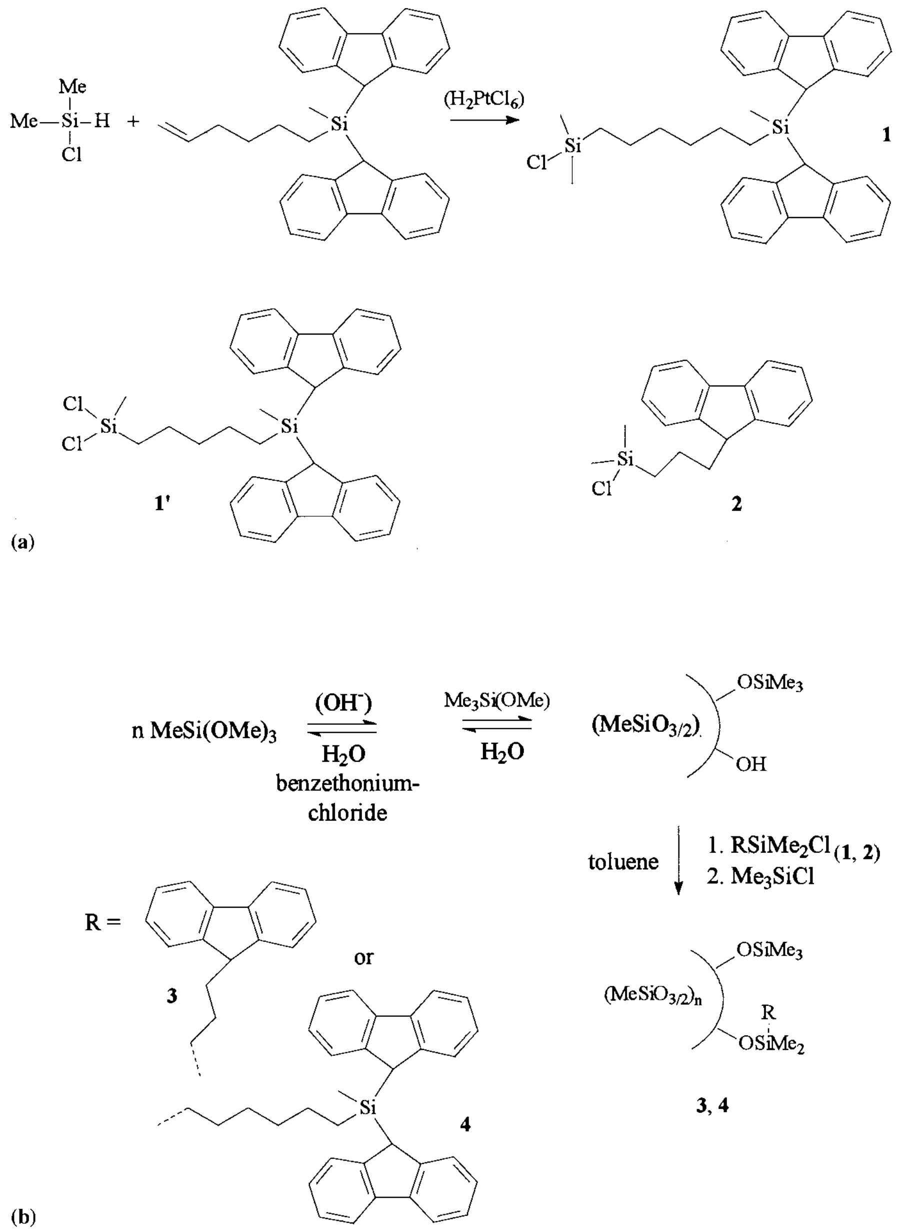
PII S0022-328X(98)00841-9

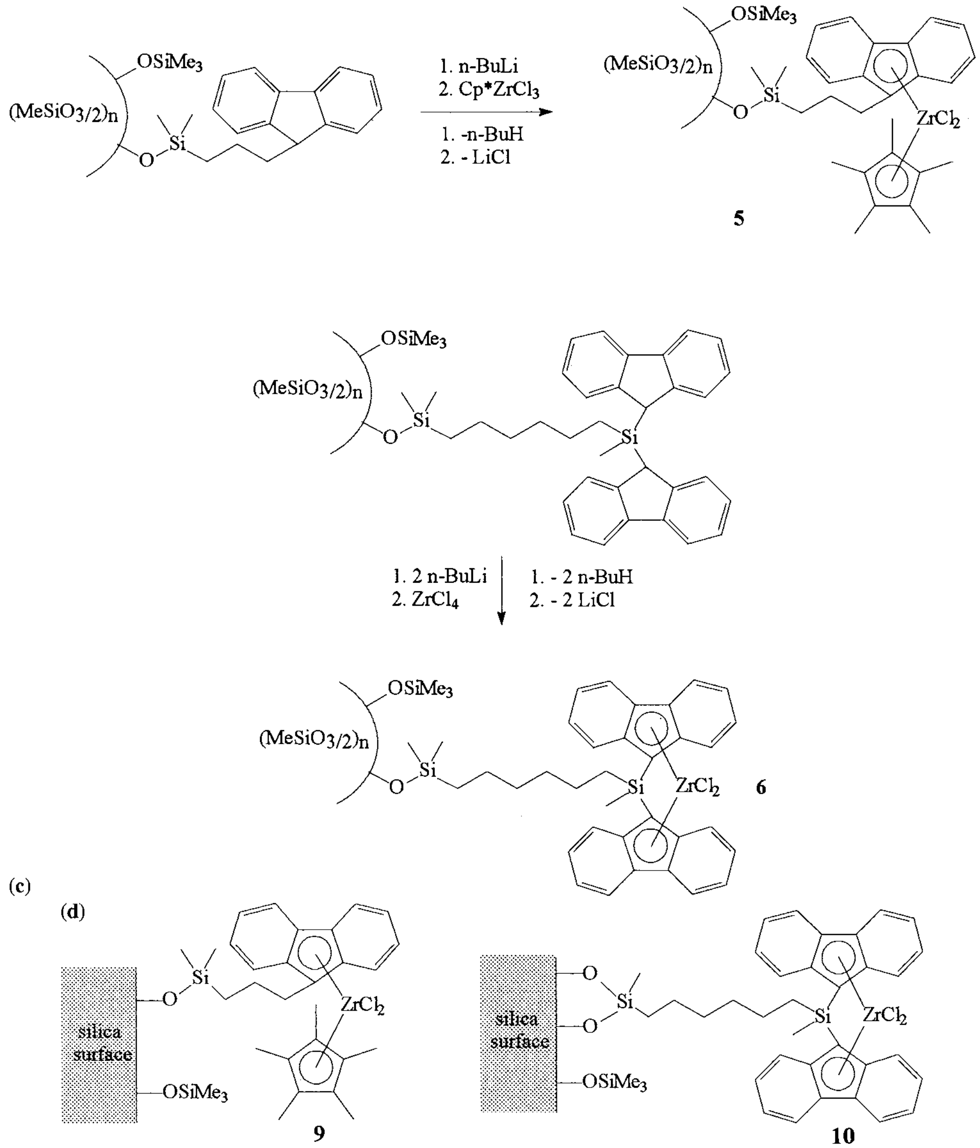


Scheme 1. (a) Synthesis of ligand precursor **1** (the analogous route was used for the preparation of ligand precursors **1**′ and **2**). (b) Synthesis of micro gel immobilized ligand precursors **3** and **4**. (c) Synthesis of micro gel immobilized catalyst precursors **5** and **6**. (d) Silica supported catalyst precursors **9** and **10**.

For comparison the homogeneous and silica supported counterparts have been synthesized. The preparation of the micro gel and silica supported metallocene catalyst precursors exhibits first a multistep reaction to build the functionalized catalyst support and second to form the metal complex. The syntheses of the micro gel supported catalyst precursors are given in Scheme 1(a–d). The analogous silica supported metallocene dichloride compounds were similarly prepared by the reaction of **2** and **1**′ with silica forming the ligand precursors **7** and **8**, followed by the subsequent treatment with *n*-BuLi, Cp^*ZrCl_3 and $ZrCl_4$, respectively, to form the catalyst precursors **9** and **10**.

The products were characterized by NMR spectroscopy and elemental analysis. Further the ligand precursor functionalized micro gels were characterized by light scattering in *n*-heptane at 25°C. The results are shown in Tables 1–3.

Compounds **3** and **4** exhibit a ligand precursor concentration of 0.07 (support) and 0.12 mmol g^{-1}, respectively. The molecular weights of the functionalized micro gels vary from 16.8 (**3**) to 10.2 kg mol^{-1} (**4**). The zirconium content of the micro gel supported catalyst precursors was found to be 1.53 (**5**) and 3.74 (**6**) (w/w), in the case of silica 3.48 (**9**) and 0.22 (**10**) (w/w).



Scheme 1. (*Continued*)

The immobilization of metallocene dichloride complexes on silica and polyorganosiloxane micro gels both leads to catalyst precursors which show a fairly good activitiy when activated with MAO at low Al/Zr molar ratios (Table 4).

Nevertheless, the homogeneously effective catalysts show a much higher polymerization activity but at higher Al/Zr ratio and with strong reactor fouling. The lower activities are due to Locatelli's [30] results and are assigned to side reactions which appear during the synthesis of the immobilized metallocene complexes. This decreased number of potential active centers results in lower polymerization activities.

The catalyst precursors immobilized on micro gel and silica exhibit a similar polymerization behavior after activation with MAO. The activities are in a narrow range from 0.14 to 1.44 kg PE g^{-1} Zr h^{-1}. In general, the molecular weights of the polyethylenes produced by the heterogeneously active catalysts are significantly higher than those made with their homogeneous counterparts (Scheme 2).

This is due to the assumption of a sterically hindered β-H-elimination, which on the other hand (**11**, **12**) can proceed without the influence of a bulky support. There is no obvious trend in the melting points of the resulting polymers.

3. Experimental

3.1. Materials

Trimethylmethoxysilane and methyltrimethoxysilane were donated from Wacker-Chemie GmbH, Burg-

Table 1
NMR data of compounds **1**–**4**,**11**,**12** (in $CDCl_3$ at 25°C)

	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	^{29}Si-NMR δ (ppm)[a]
1	0.33 (s; 3H), 0.32 (m; 2H), 0.42 (s; 6H), 0.57 (m; 2H), 0.74 (m; 2H), 0.92–1.10 (m; 4H), 1.25 (m; 2H), 4.16 (s; 2H), 7.28–7.48 (m; 12H), 7.90 (d, $^3J(^1H,^1H) = 7.5$ Hz; 4H)	−7.1 (CH_3), 1.7 (CH_3), 11.6 (CH_2), 18.9 (CH_2), 22.7 (CH_2), 23.1 (CH_2), 32.2 (CH_2), 32.9 (CH_2), 39.7 (CH), 120.1 (CH), 124.3 (CH), 125.6 (CH), 126.2 (CH), 140.7 (C_q), 145.0 (C_q)	7.0 [6.6], 32.2 [7.5]
1′	0.33 (s; 3H), 0.27–0.34 (m; 2H), 0.58 (br; 2H), 0.79 (s; 3H), 0.94–1.07 (m; 6H), 1.31 (m; 2H), 4.18 (br; 2H), 7.31–7.51 (m; 12H), 7.89–7.94 (m; 4H)	−7.2 (CH_3), 5.0 (CH_3), 11.6 (CH_2), 23.0 (CH_2), 22.1 (CH_2), 21.6 (CH_2), 31.6(CH_2), 32.7 (CH_2), 39.7 (CH), 120.1 (CH), 124.3 (CH), 125.6 (CH), 126.2 (CH), 140.8 (C_q), 145.0 (C_q)	7.0 [6.5], 34.1 [—]
2	0.44 (s; 3H), 0.91 (m; 2H), 1.52 (m; 2H), 2.05–2.15 (m; 2H), 4.04 (t, $^3J(^1H,^1H) = 6.1$ Hz; 1H), 7.35–7.47 (m; 4H), 7.57 (d; $^3J(^1H,^1H) = 7.2$ Hz; 2H), 7.82 (d, $^3J(^1H,^1H) = 7.2$ Hz; 2H)	1.7 (CH_3), 19.1 (CH_2), 19.6 (CH_2), 36.4 (CH_2), 47.2 (CH), 119.8 (CH), 124.3 (CH), 126.8 (CH), 126.9 (CH), 141.0 (C_q), 147.3 (CH)	32.0 [7.4]
3	1.5–1.5 (br, CH_3), 0.86 (m, CH_3), 1.23 (m, CH_3), 1.57 (br, CH_3), 1.92 (br, CH_2), 3.94 (br, CH), 7.38–7.45 (br, CH), 7.62–7.75 (br, CH)	—	—
4	1.3–0.8 (br, CH_3), 0.90 (br, CH_2), 1.22 (br, CH_2), 3.43 (br, OCH_3), 4.09 (br, CH), 7.17–7.38 (br, CH), 7.83 (br, CH)	—	—
11	0.92 (t, $^3J(^1H,^1H) = 7.4$ Hz; 3H), 1.57–1.70 (m; 2H), 1.65 (s; 15H), 3.26 (t, $^3J(^1H,^1H) = 7.8$ Hz; 1H), 7.26–7.33 (m; 4H), 7.66 (dd, $^3J(^1H, ^1H = 8.5$ Hz, $^4J(^1H,^1H) = 1.0$ Hz; 2H), 8.18 (dd, $^3J(^1H,^1H) = 8.3$ Hz, $^4J(^1H,^1H) = 1.0$ Hz; 2H)	11.7 (CH_3), 14.5 (CH_3), 24.1 (CH_2), 28.3 (CH_2), 106.1 (C_q), 115.9 (C_q), 123.0 (CH), 123.4 (CH), 124.6 (CH), 125.9 (CH), 126.1 (C_q), 131.6(C_q)	—
12	0.96 (t, $^3J(^1H,^1H) = 7.1$ Hz; 3H), 1.39–1.52 (m; 4H), 1.66 (s; 3H), 1.67–1.79 (m; 2H), 1.98–2.07 (m; 2H), 2.13–2.21 (m; 2H), 7.04–7.10 (m; 4H), 7.31–7.38 (m; 4H), 7.78–7.86 (m; 8H)	0.0 (CH_3), 14.1 (CH_3), 18.3 (CH_2), 22.6 (CH_2), 23.0 (CH_2), 31.7 (CH_2), 33.4 (CH_2), 64.5 (C_q), 124.7 (CH), 125.4 (CH), 126.1 (CH), 127.7 (C_q), 127.8 (C_q), 128.3 (CH), 130.3 (C_q), 130.6 (C_q)	−12.8 [—]

[a] $^2J(^{29}Si,^1H)$ [Hz].

Table 2
Analytical data of compounds **3** and **4**

Compound	M_w (kg mol^{-1})	r_h (nm)	r_g (nm)	ρ (g cm^{-3})	Ligand precursor concentration (mmol g^{-1})
3	16.8	31.0	42.5	1.37	0.07
4	10.2	14.9	23.8	1.60	0.12

hausen, Germany, and used without further purification. All other silanes were commercially available and were distilled in vacuo for purification prior to use. Methylaluminoxane was donated by Witco GmbH, Bergkamen, Germany, and used without further purification. Ethylene was purchased in technical grade from Linde AG, Germany, and purified by passing it through an alumina column.

Toluene, pentane and diethylether were purchased in technical grades and purified by distillation from Na/K alloy under argon atmosphere. All other chemicals were commercially available or have been synthesized according to literature procedures.

3.2. Syntheses of functionalized polysiloxane micro gels

A 10.00 g (22.3 mmol) sample of benzethonium chloride and a solution of sodium hydroxide (10 (w/w); 1.0 ml, 2.5 mmol) were dissolved in 500 ml water. 104.7 ml (734.0 mmol) trimethoxymethylsilane were added at room temperature (r.t.) during 3 h of vigorous stirring. The resulting dispersion was stirred for additional 12 h at r.t.

A total of 5.3 ml (38.6 mmol) of methoxytrimethylsilane were added to a portion of 100 g of the obtained clearly opalescent dispersion. The resulting mixture was stirred for additional 12 h, precipitated by pouring it into 250 ml methanol and filtered. The sludge was washed several times with portions of 50 ml methanol and dissolved in 150 ml toluene. The solution was poured again into 200 ml methanol, the polymer was filtered and washed again with five portions of 50 ml methanol. The isolated wet polysiloxane was dissolved in 150 ml toluene and the solution was concentrated by vacuum distillation.

Table 3
Zirconium content of compounds **5**,**6**,**9**,**10**

Compound	Zr content (weight %)
5	1.53
6	3.74
9	3.48
10	0.22

*3.2.1. Fluorenyl substituted polymethylsiloxane micro gel (**3**)*

To the remaining clearly opalescent micro dispersion, 3.01 g (10.0 mmol) 3-(9-fluorenyl)propyldimethylchlorosilane were added. After a stirring period of 12 h at r.t., 3.8 ml (30.0 mmol) trimethylchlorosilane were added and stirred for additional 12 h. The solution was dropped into 200 ml methanol, the precipitate was filtered and dried in vacuo for 24 h at r.t.

*3.2.2. Bridged bis(fluorenyl) substituted polymethylsiloxane micro gel (**4**)*

A 5.51 g (10.0 mmol) sample of bis(9-fluorenyl)-6-(chlorodimethylsilyl)-1-hexylmethylsilane was added to the opalescent dispersion. After a stirring period of 12 h at r.t., 3.8 ml (30.0 mmol) trimethylchlorosilane were added and stirred for additional 12 h. The solution was poured into 200 ml methanol, the precipitate was filtered and the white sludge was dried in vacuo for 24 h.

3.3. Syntheses of functionalized silicas

*3.3.1. Fluorenyl functionalized silica (**7**)*

A total of 5.00 g of pretreated silica (Merck 7734), heated at 600°C for 60 min under constant O_2 flow and cooled under Ar, were slurried in a solution of 3.10 g (10.0 mmol) 3-(9-fluorenyl)propyldimethylchlorosilane and 20.0 ml (144.0 mmol) triethylamine in toluene for 2 h. 16.4 ml (130.0 mmol) chlorotrimethylsilane were added and the slurry was stirred for additional 8 h. Excess triethylamine and amine hydrochloride were removed by repeated decanting of a silica toluene slurry. The obtained fluorenyl functionalized silica was washed successively with toluene, ether and pentane and dried in vacuo for 12 h.

*3.3.2. Bridged bis(fluorenyl) functionalized silica (**8**)*

A slurry of 5.00 g pretreated silica (Merck 7734) in 100 ml toluene and a solution of 5.51 g (10.0 mmol) bis(9-fluorenyl)-6-(chlorodimethylsilyl)-1-hexylmethylsilane and 20.0 ml (144.0 mmol) triethylamine in 100 ml toluene were combined and stirred for 2 h. Subsequently 16.4 ml (130.0 mmol) chlorotrimethylsilane were added and the slurry was stirred for additional 8 h. Excess triethylamine and amine hydrochloride were removed by repeated decanting of a silica toluene

Table 4
Ethylene polymerization results

Catalyst	[Zr]/[Al] (molar ratio)	Activity [g PE × (mmol M·h)$^{-1}$]^{a}	$\bar{M}_{\eta}$ (10^3 g·mol^{-1})	T_m (°C)^{b}
5/MAO	1:600	700	395	142.2
6/MAO	1:50	140	1230	138.0
9/MAO	1:150	150	540	136.8
10/MAO	1:1400	1440	640	135.8
11/MAO	1:8000	15 500	180	142.5
12/MAO	1:8000	84 800	540	138.2

[a] $T_P = 60$°C, in pentane, terminated after 1 h. [b] Maximum of melting peak during second heating (DSC).

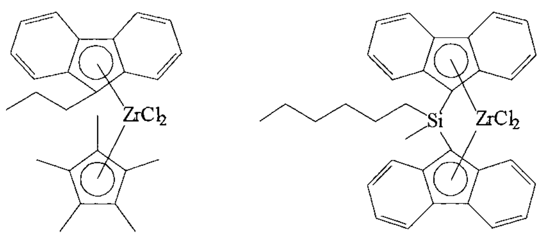
slurry. The obtained bis(fluorenyl) functionalized silica was successively washed with toluene, ether and pentane and dried in vacuo for 12 h.

3.4. Syntheses of supported catalyst precursors

3.4.1. Synthesis of micro gel supported catalyst precursor

*3.4.1.1. Unbridged metallocene dichloride compound **5**.* A 1.00 g (0.07 mmol) sample of compound **3** was dissolved in 50 ml diethylether, 0.44 ml (0.7 mmol) *n*-buthyllithium were added and stirred for 2 h at r.t. 0.11 g (0.33 mmol) (η^5-pentamethylcyclopentadienyl)zirconium trichloride were added and stirred for another 10 h at r.t. After precipitation of the solid, the solution was decanted, washed five times with 50 ml diethylether and dried in vacuo for 24 h at r.t. Yield: 0.23 g (**5**) as a slightly yellow powder.

*3.4.1.2. Bridged ansa-metallocene dichloride compound **6**.* To a solution of 1.56 g (0.19 mmol) of **4** in 70 ml diethylether 1.56 ml (2.50 mmol) *n*-buthyllithium were added and stirred for 2 h at r.t. Then 0.23 g (1.0 mmol) zirconium tetrachloride were added and stirred for another 12 h at r.t. After precipitation of the solid, the solution was decanted, washed five times with 50 ml diethylether and dried in in vacuo for 24 h at r.t. Yield: 0.98 g (**6**) as a colorless powder.



11 **12**

Scheme 2. Catalyst precursors **11** and **12** for homogeneous polymerization.

3.4.2. Synthesis of silica supported catalyst precursor

The ligand precursor **7**/**8** (1.50 g, assumption: 1.0 mmol ligand precursor g^{-1} silica) was slurried in 50 ml diethylether and the equimolar amount of *n*-butyllithium (1.6 M in *n*-hexane) was added. After stirring for 2 h at r.t., 0.50 g (1.5 mmol) pentamethyl-cyclopentadienylzirconium trichloride or 0.35 g (1.5 mmol) zirconium tetrachloride, respectively, were added to the slurry and vigorously shaken for 12 h at r.t. After precipitation of the solid, the solution was decanted, washed five times with 50 ml diethylether and dried in vacuo for 24 h at r.t. Yield: 1.02 g (**9**) as a slightly yellow solid and 0.57 g (**10**) as a pink solid, respectively.

3.5. Syntheses of metallocene dichloride complexes

(η^5-Pentamethylcyclopentadienyl)(η^5-9-propylfluorenyl)zirconium dichloride, Cp*(9-^{n}PrFlu)$ZrCl_2$ (**11**), was prepared according to literature [31]. A 0.83 g (4 mmol) sample of 9-propylfluorene was lithiated with 2.5 ml (4 mmol) *n*-butyllithium in diethylether at −75°C and reacted with 1.33 g (4 mmol) Cp*$ZrCl_3$ for 8 h at r.t. The resulting orange suspension was filtered from LiCl, the obtained solution was evaporated and crystallized after resolving in toluene. Compound **11** was isolated as orange needles in 51% yield.

Bis(η^5-9-fluorenyl)-1-hexylmethylsilane zirconium dichloride (**12**) was prepared according to literature procedure [32] by lithiating 4.59 g (10 mmol) bis(9-fluorenyl)-1-hexylmethylsilane in 100 ml diethylether at − 78°C with 12.5 ml (20 mmol) *n*-butyllithium and reacting the resulting dianion with 2.33 g (10 mmol) $ZrCl_4$ for 20 h at r.t. The reaction mixture was evaporated, the residue extracted with toluene and crystallized at − 78°C. Compound **12** was isolated in 47% yield as deep red powder.

3.6. Polymerization and analytical procedures

The polymerization of ethylene was conducted in a 1 l Büchi steel reactor equipped with a mechanical stirrer at 60°C and 10 bar ethylene pressure for 1 h using pentane as diluent and 30 w/w MAO solution in toluene as cocatalyst. The polymerization was stopped by venting excess ethylene. The obtained polymer was adequately washed with HCl/methanol and dried in vacuo at 50°C for 14 h.

The molecular weight was determined by viscosimetry in a Ubbelohde capillary viscometer at 135°C using decaline as solvent. Differential scanning calorimetry measurements were conducted using a Netzsch DSC 200 at a heating rate of 20 K min^{-1}.

NMR data were obtained using a Bruker ARX 250 spectrometer at 25°C in $CDCl_3$ or CD_2Cl_2. IR spectra within a range 4000–600 cm^{-1} were obtained with a Bruker IFS 66v spectrometer using diffuse reflection techniques. Concentration of immobilized ligand precursors at micro gel surfaces were determined by means of UV spectroscopy (Cary 17 DX) in heptane at 20°C.

Acknowledgements

This work was supported by the Bayerischer Forschungsverbund Katalyse (FORKAT) and Wacker-Chemie GmbH.

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