Zirconium β-diketonate/methylaluminoxane systems as single-site catalysts for the preparation of high-molecular-weight polyethylene

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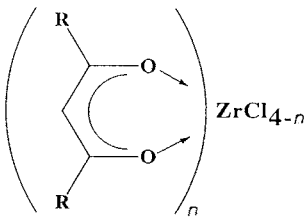
Introduction

In view of the high academic and industrial interest in metallocene/methylaluminoxane systems as a new generation of Ziegler-Natta catalysts[1–6], we report here the use of methylaluminoxane (MAO) as a cocatalyst for the activation of molecular zirconium β-diketonate complexes **1** in the polymerization of ethylene. Titanium tetrakis(acetylacetonate) as well as acetylacetone itself have been included in the early patent literature for the polymerization of α-olefins with alkylaluminium compounds as cocatalysts[7–9]. A recent patent on olefin polymerizations with ZrL_2Cl_2—MAO (L = β-diketonate, i.e. **1** with $n = 2$)[10] and a report from Longo et al. on the polymerization of styrene with ZrL_2Cl_2/MAO[11], both of which appeared during the course of our study, prompt us to report our results with **1**-MAO and **1**-MAO-TMA (TMA = trimethylaluminium).



1

R = CH_3:
Acetylacetonate complexes:
$(acac)_nZrCl_{4-n}$

R = C_6H_5:
Dibenzoylmethanate complexes:
$(dbm)_nZrCl_{4-n}$

Experimental part

Materials

The zirconium chelate complexes **1** were prepared according to literature procedures[12, 13]. The complex $(dbm)_2ZrCl_2(THF)$ precipitated upon dissolution of $(dbm)_2ZrCl_2$ in tetrahydrofuran (THF). Dicyclopentadienylzirconium dichloride (Cp_2ZrCl_2) was purchased from Merck, and methylaluminoxane (MAO) was obtained from Witco (Bergkamen, Germany) as a 10 wt.-%

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toluene solution (4,92 wt.-% aluminium, density ≈ 0,9 g/mL, average molar mass of the MAO oligomers 900 – 1 100 g/mol). Trimethylaluminium (TMA) was used as a 2 molar toluene solution from Aldrich. Toluene was refluxed over sodium metal for several hours, followed by distillation and storage under argon. Ethylene (BASF AG) was polymerization-grade and used without further purification.

Molecular weights and molecular weight distributions of the polyethylenes were determined using gel-permeation chromatography (GPC, Waters 150 chromatography) at 135 °C, solvent 1,2,4-trichlorobenzene.

Polymerizations

Polymerizations were carried out in a 1 L Büchi-glass autoclave, thermostated to 70 °C and charged with 300 mL toluene, MAO, alone or with TMA, and the transition metal complex. The catalyst amount, concentration and mole ratio Al : Zr is specified in Tabs. 1 and 2. After an activation time of 10 min the autoclave was pressurized with 5 bar ethylene and after 1 h the reaction was stopped by draining the toluene/polyethylene slurry into acidified water. The polymer was separated by filtration, washed with hexane and dried at 80 °C. To ensure reproducibility the polymerizations were carried out at least twice with each zirconium complex.

Results and discussion

The catalyst productivities and properties of polyethylenes obtained with the catalyst systems **1**-MAO are listed in Tab. 1.

The productivities of the zirconium chelates are somewhat lower than that of the metallocene-type zirconocene dichloride[a], yet the molecular weights of the polymers obtained are considerably higher, suggesting a slow chain-termination reaction relative to chain propagation. The molecular weight distribution (MWD) of the polymer is rather narrow, thus, indicating high uniformity or single-site character of the active species. The slight broadening of the MWD can be ascribed to polymer precipitation which rapidly leads to a heterogeneous phase, i. e. a diffusion-controlled reaction. The polymerization is truly homogeneous only in the very beginning[17].

When part of the MAO cocatalyst is replaced by TMA a strong increase in productivity can be observed with the zirconium chelate complexes, thereby approaching the productivity of the Cp_2ZrCl_2 reference. The polymerization results with the systems **1**-MAO-TMA are summarized in Tab. 2.

A similar MAO/TMA replacement in the system Cp_2ZrCl_2/MAO did not lead to appreciable changes in the polymer yield[18]. We note that **1** cannot be activated by TMA alone towards the polymerization of ethylene.

From the activity of complexes of **1** with $n = 4$ it is evident that the chelate ligands can be replaced by methyl groups from MAO or TMA to give an active species with an opening in the coordination sphere for the ethylene monomer. While **1**-MAO gives catalysts which differ only slightly in activity for the two ligand types and various numbers n, a greater diversity is achieved in combination with TMA. The origin of this diversity and the nature of the active species will be the subject of future investigations.

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[a] The polymerization activities reported here for Cp_2ZrCl_2/MAO are much lower than those given by Kaminsky et al.[14–16]. This is due to the higher metallocene concentration and lower (more economically feasable) mole ratio Al : Zr employed by us (see also ref.[17]).

Tab. 1. Polymerization of ethylene with catalytic systems consisting of zirconium chelate complexes **1** and methylaluminoxane (MAO) in 300 mL toluene with $3 \cdot 10^{-6}$ mol of the complex, and $12 \cdot 10^{-3}$ mol MAO, equivalent to [Zr] = 10^{-5} mol/L and a mole ratio of Al : Zr = 4000 : 1 at 70 °C

Zirconium complex[a]	Yield[b]	Productivity[c]	$\bar{M}_w$[d]	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$
Cp_2ZrCl_2	29,9	21,9[f]	78900	27800	2,84
$(acac)_4Zr$	15,6	11,4	414500	136000	3,05
$(acac)_3ZrCl$	14,8	10,8	438700	156800	2,80
$(acac)_2ZrCl_2$	14,5	10,6	563200	215300	2,62
$(dbm)_4Zr$	16,2	11,8	301000	82000	3,67
$(dbm)_3ZrCl$	12,7	9,3	391000	124100	3,15
$(dbm)_2ZrCl_2$	17,0	12,4	242500	82600	2,94
$(dbm)_2ZrCl_2(THF)$	16,7	12,2	336500	97600	3,45

[a] Cp_2ZrCl_2 = dicyclopentadienylzirconium dichloride; Hacac = acetylacetone (2,4-pentanedione); Hdbm = dibenzoylmethane (1,3-diphenyl-1,3-propanedione); THF = tetrahydrofuran.
[b] In g of polyethylene (PE).
[c] In units kg PE per g Zr per h per bar.
[d] Weight-average molecular weight.
[e] Number-average molecular weight.
[f] See footnote[a] previous page.

Tab. 2. Polymerization of ethylene with catalytic systems consisting of zirconium chelate complexes **1** and MAO/TMA in 300 mL toluene with $3 \cdot 10^{-6}$ mol of the complex, $6 \cdot 10^{-3}$ mol MAO, and $6 \cdot 10^{-3}$ mol TMA equivalent to [Zr] = 10^{-5} mol/L and a mole ratio of $Al_{MAO} : Al_{TMA} : Zr$ = 2000 : 2000 : 1 at 70 °C[a]

Zirconium complex[a]	Yield[b] in g PE	Productivity[c]	$\bar{M}_w$[d]	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$
Cp_2ZrCl_2	31,3	22,9[f]	170200	53600	3,18
$(acac)_4Zr$	24,9	18,2	401500	130000	3,09
$(acac)_3ZrCl$	24,7	18,1	144000	66300	2,17
$(acac)_2ZrCl_2$	14,8	10,8	494000	187300	2,64
$(dbm)_4Zr$	25,4	18,6	188000	80600	2,33
$(dbm)_3ZrCl$	36,7	26,8	238600	85700	2,78
$(dbm)_2ZrCl_2$	19,6	14,3	519200	166600	3,12
$(dbm)_2ZrCl_2(THF)$	18,1	13,2	414000	142300	2,91

[a] See corresponding footnotes in Tab. 1.

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