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The influence of methylalumoxane concentration on propene polymerization with homogeneous metallocene-based Ziegler–Natta catalysts ☆

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Abstract

Propene polymerization using homogeneous methylalumoxane (MAO)-activated *rac*-$Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$ was studied as a function of both metallocene and MAO concentration. At 40 °C and 2 bar propene pressure in toluene the catalyst activities and poly(propene) molecular weights depend upon the MAO concentration, whereas the zirconium concentration and the [Al]/[Zr] molar ratios are much less significant. At high MAO concentrations, MAO competes with propene for vacant coordination sites, thus adversely affecting catalyst activity. Optimum performance in terms of catalyst activity and molecular weight was obtained at an MAO concentration with $[Al] = 5$ mmol l^{-1}.

Keywords: Ziegler–Natta catalysts; Methylaluminoxane; Propene polymerization

1. Introduction

Since Sinn and Kaminsky [1b] have identified methylalumoxane (MAO) as an effective cocatalyst for the activation of metallocene-based Ziegler–Natta catalysts, much research effort has been devoted to achieving a better understanding of the role of MAO cocatalyst and MAO interactions with metallocenes. According to the currently accepted mechanistic scheme [2], MAO alkylates metallocenes and affords cationic metallocenes by abstracting and complexing the counter-ion. This is in accord with the observation that MAO-free cationic metallocene catalysts based on metallocene alkyls and strong Lewis acids [3], e.g. $[Me_2SiInd_2ZrR]^+[RB(C_6F_5)_3]^-$, are also active catalysts [4]. Moreover, MAO scavenges catalyst poisons. At present it is not fully understood why a large excess of MAO relative to the metallocene, with an [AL] [mettalocene] molar ratios ranging between 500 and 10000, is required to achieve high catalyst activities. Data in the literature concerning the influence of MAO are often conflicting. For instance the catalyst activity of Cp_2ZrCl_2–MAO in ethene [5] and propene [6] polymerization increased steadily with increasing [Al]/[Zr] molar ratio. In contrast, Herfert and Fink [7] identified the existence of an optimum [Al]/[Zr] molar ratio with maximum polymerization rate when ethene and propene were polymerized with $Me_2SiInd_2ZrCl_2$–MAO, $Me_2C(Cp)(Flu)ZrCl_2$–MAO and $Me_2C(3\text{-}Me\text{-}Cp)(Flu)ZrCl_2$–MAO. At higher [Al]/[Zr] molar ratios the catalyst activity decreased markedly. In view of improving the economics of metallocene catalysts it is important to reduce the demand of expensive MAO cocatalysts. Therefore the objective of our research has been to clarify the role of [Al]/[Zr] molar ratios as well as of the MAO and metallocene concentrations in propene polymerization using the highly active and stereoselective *rac*-$Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$–MAO catalyst.

2. Results and discussion

Brintzinger and coworkers [8a] and Spaleck et al. [86] have discovered that substitution in the 2- and

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☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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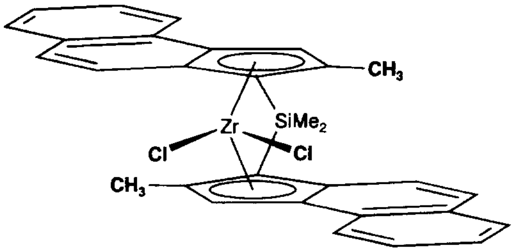

Scheme 1. *rac*-$Me_2Si(2\text{-Me-Benz[e]Indenyl})_2ZrCl_2$.

4-position of silylene-bridged bisindenylzirconocenes leads to Ziegler–Natta catalysts which afford high molecular weight poly(propene) with high yields with respect to the transition metal. In this study we investigated the effect of MAO concentration on the performance of MAO-activated *rac*-$Me_2Si(2\text{-Me-Benz[e]Ind})_2ZrCl_2$ (Scheme 1). Propene polymerization was performed in toluene at 40 °C and 2 bar propene pressure, which was maintained by feeding propene during polymerization. Pre-activated catalyst, comprising a metallocene–MAO–toluene solution, was injected into MAO–toluene solution saturated with propene to initiate polymerization.

In Fig. 1, propene polymerization activities, corresponding to [Al] concentrations of 2.5, 5, 10, and 20 mmol l^{-1} and [Zr] concentrations of 1 and 2 μmol l^{-1}, are plotted against time. While the zirconium concentration did not affect propene the polymerization activity–time functions, the total [Al] concentration was much more important than the [Al]/[Zr] molar ratios. At [Al] = 20 mmol l^{-1} (curves d in Fig. 1) a constant high polymerization activity of approximately 30 t poly(propene) (mol zircon)$^{-1}$ (mol propene l^{-1})$^{-1}$ h^{-1} was obtained immediately after injecting the pre-activated catalyst solution for both zirconocene concentrations of [Zr] = 1 and 2 μmol l^{-1} although these two runs have different [Al]/[Zr] molar ratios of 20000 and 10000 respectively.

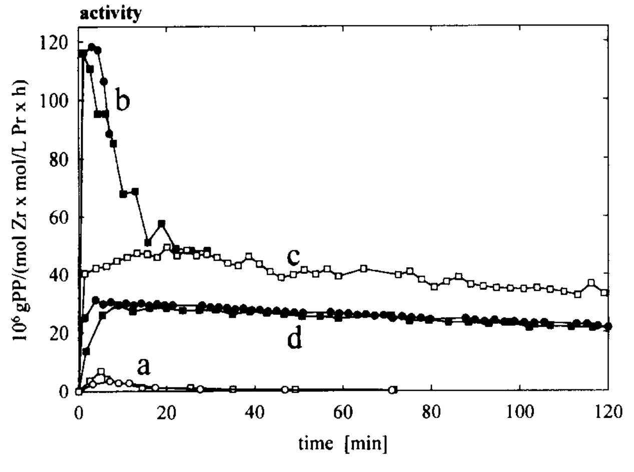

Fig. 1. Catalyst activities of $Me_2Si(2\text{-Me-Benz[e]Ind})_2ZrCl_2$–MAO at different MAO and Zr concentrations: curve a, □, [Al] = 2.5 mmol l^{-1}, [Zr] = 1 μmol l^{-1}, [Al]/[Zr] = 2500, run 132; curve a, ○, [Al] = 2.5 mmol l^{-1}, [Zr] = 2 μmol l^{-1}, [Al]/[Zr] = 1250, run 134; curve b, ■, [Al] = 5 mmol l^{-1}, [Zr] = 1 μmol l^{-1}, [Al]/[Zr] = 5000, run 131; curve b, ●, [Al] = 5 mmol l^{-1}, [Zr] = 2 μmol l^{-1}, [Al]/[Zr] = 2500, run 133; curve c, □, [Al] = 10 mmol l^{-1}, [Zr] = 1 μmol l^{-1}, [Al]/[Zr] = 10000, run 120; curve d, ■, [Al] = 20 mmol l^{-1}, [Zr] = 1 μmol l^{-1}, [Al]/[Zr] = 20000, run 82; curve d, ●, [Al] = 20 mmol l^{-1}, [Zr] = 2 gmmol l^{-1}, [Al]/[Zr] = 10000, run 81.

At [Al] = 10 mmol l^{-1} the catalyst activity increased to 49 t poly(propene) (mol zircon)$^{-1}$ (mol propene l^{-1})$^{-1}$ h^{-1}, as can be seen from curve c in Fig. 1, whereas curves b in Fig. 1 show that at [Al] = 5 mmol l^{-1} the drastically increased initial catalyst activities of about 120 t poly(propene) (mol zircon)$^{-1}$ (mol propene l^{-1})$^{-1}$ h^{-1} were accompanied by a significant catalyst activity decay with time. This extraordinary high yield of poly(propene) with rather low bulk density (see Table 1) that did not permit stable operation. Polymerization had to be stopped after 10 and 30 min owing to stirring problems.

At [Al] = 2.5 mmol l^{-1} (curves a in Fig. 1) the catalyst activity was very poor. Interestingly, at the same [Al]/[Zr] molar ratio of 2500, a low catalyst activity (run 132 in Fig. 1 and Table 1) and a very high catalyst activity (run 133 in Fig. 1 and Table 1) were obtained. Clearly, the total [Al] concentration appeared to be a much more important parameter when compared with the [Al]/[Zr] molar ratios and total [Zr] concentration. Observations of polymerization activity maxima are in accord with those reported by Herfert and Fink [7] for propene polymerization with $Me_2SiInd_2ZrCl_2$–MAC–toluene for different [Al]/[Zr] ratios which are equivalent to markedly varied [Al] concentrations. Moreover, these data are in line with our previous finding [9] that when polymerizing at different temperatures with [Al] = 20 mmol l^{-1} the [Zr] concentration, varied between 1 and 2 μmol l^{-1}, did not affect either the polymerization kinetics or the poly(propene) properties.

For further clarification of the role of [Al] concentration, MAO was injected during propene polymerization with the low activity catalyst comprising [Zr] = 1 μmol l^{-1} and [Al] = 2.5 mmol l^{-1}. As is apparent in Fig. 2, MAO injection, increasing the [Al] concentration from 2.5 to 8.6 mmol l^{-1}, was accompanied by a more than tenfold higher polymerization activity. While at low [Al] concentration the catalyst activity decayed with time, the high polymerization activity was constant for several hours after MAO injection.

Table 1 lists the properties of poly(propenes) prepared at different MAO concentrations. The poly(propene) molecular weight, determined by means of viscosity measurements, depends also on the MAO concentration. As displayed in Fig. 3 and Fig. 4, both the polymerization rate and the poly(propene) molecular weights exhibit maximum values at [Al] = 5 mmol l^{-1}. Variation in the zirconocene concentration from [Zr] = 1

Table 1
Influence of methylalumoxane concentration on propene polymerization using $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$ /MAO [a]

Run	[Al] (mmol l^{-1})	[Zr] (μmol l^{-1})	[Al]/[Zr] molar ratio	Activity [b] (g × 10^6 poly-(propene) (mol Zr)$^{-1}$ (mol propene $L^{-1})^{-1}$ h^{-1})	M_n (from size exclusion chromatography (kg mol^{-1})	M_n / M_n (from size exclusion chromatography Viscos.	M_{vis} (from viscosity measurements) (kg mol^{-1})	M_n [c] (from ^{1}H NMR) (kg mol^{-1})	ρ_{bulk} [d] (g ml^{-1})	T_m (°C)	[*mmmm*] (%)	2,1 units [e] (%)
134	2.5	2	1250	4	175	2.1	335	60	0.09	151.7	94.4	0.5
132	2.5	1	2500	7	91	3.5	285	50	ND [f]	149.9	94.4	0.5
133	5	2	2500	118	194	1.9	340	120	0.06	154.5	95.8	0.3
131	5	1	5000	116	213	2.0	420	140	0.07	156.7	96.1	0.3
120	10	1	10000	49	209	1.9	299	110	0.10	155.7	96.0	0.3
81	20	2	10000	31	127	1.7	198	100	0.10	155.4	96.1	0.4
82	20	1	20000	30	138	1.7	208	120	0.11	155.4	96.6	0.3

[a] At 40°C, 2 bar total pressure; total pressure = propene partial pressure + toluene partial pressure; [propene] = 0.91 mol L^{-1}; toluene, 615 ml.

[b] Maximum activity, 10^6 g poly(propene) (mol zircon)$^{-1}$ (mol propene $L^{-1})^{-1}$ h^{-1}; see Fig. 1.

[c] Estimated by ^{1}H NMR on basis of the vinylidene end group.

[d] Bulk density of the poly(propene) powder.

[e] By ^{13}C NMR; average intensity of signals from 2,1 units in percentage of total methyl-pentad intensity

[f] ND, not determined owing to an insufficient amount of material.

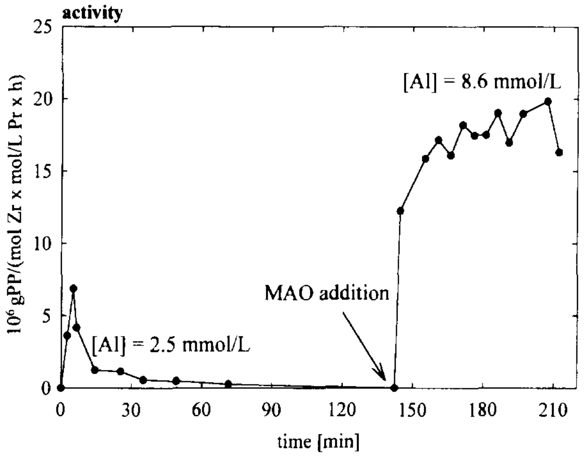

Fig. 2. Catalyst activities of $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$–MAO at different MAO concentrations (MAO addition during one polymerization run).

to 2 μmol l^{-1} has no effect on the poly(propene) molecular weight. The lowest bulk density is found for the ex-reactor poly(propene) powder with the highest molecular weight.

The only detectable poly(propene) end group is the vinylidene end group found in the ^1H NMR spectra. Moreover, the number-averaged molecular weights estimated from the intensity of the vinylidene end group show the same dependence on MAO concentration as the molecular weights measured by viscosimetry. This indicates that the [Al] concentration must influence the ratio of the polymerization rate constants of chain propagation vs. chain termination via β-hydride elimination.

Poly(propene) regioirregularities and stereoirregularities were analyzed by means of ^{13}C NMR spectroscopy. At $[Al] \geqslant 5$ mmol l^{-1} there is no effect of [Al] concentration on stereoregularity and regioregularity. Only for the low activity polymerizations at $[Al] = 2.5$ mmol l^{-1} was a small drop of tacticity and regioregularity was detected. This is reflected in the lower melting points of the poly(propenes) produced at $[Al] = 2.5$ mmol l^{-1} (T_m = 149.9 and 151.7 °C) in comparison with those found at higher [Al] concentrations (T_m = 155.4–156.7 °C).

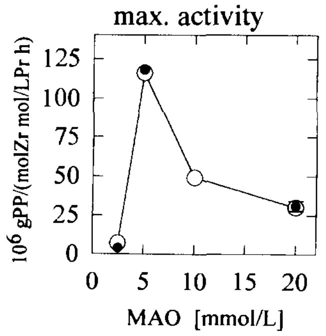

Fig. 3. Maximum catalst activities of $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2$ $ZrCl_2$–MAO at different MAO and Zr concentrations: ○, $[Zr] = 1$ μmol l^{-1}; ●, $[Zr] = 2$ μmol l^{-1}.

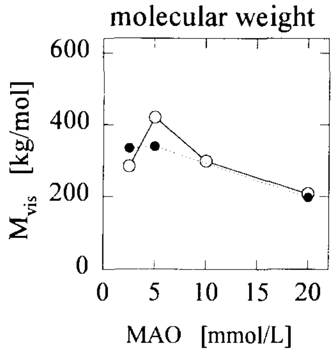

Fig. 4. Molecular weight of poly(propene) produced with $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$–MAO at different MAO and Zr concentrations: ○, $[Zr] = 1$ μmol l^{-1}; ●, $[Zr] = 2$ μmol l^{-1}.

In conclusion, the [Al] concentration influenced predominantly the molecular weight and polymerization rate, while regioirregularities and stereoregularities are unaffected at higher [Al] concentrations.

The effect of the MAO concentration on the catalyst activity is of the same magnitude as the increase in catalyst activity with increasing propene concentration reported earlier [9] for the polymerization of propene with the same catalyst at the high MAO concentration of $[Al] = 20$ mmol l^{-1}.

Variation in the [Al] and [Zr] concentrations and [Al]/[Zr] molar ratios clearly indicates that the [Al] concentration is the most important parameter in propene polymerization, having control over the polymerization rate and molecular weights. At high [Al] concentrations, exceeding 5 mmol l^{-1}, MAO is likely to convert most metallocenes into the active cationic metallocenes. However, at a high excess of MAO it may be that one of the components of the complex mixture MAO, comprising alumoxane oligomers and free of associated trimethylaluminum, competes with the olefin for the vacant coordination site of the cationic metallocene by coordination via alkyl groups or oxygen [10]. Coordination of MAO would lead to polymerization-inactive metallocene-terminated poly(propenes) which can undergo chain termination via β-hydride elimination. This would explain why at a high [Al] concentration the molecular weight, reflecting the ratio of rate constants of chain propagation and chain termination, decreased.

At a low MAO concentration with $[Al] < 5$ mmol l^{-1}, two factors may account for the poor catalyst activity and low molecular weight. On the one hand, a low MAO concentration could be insufficient to scavenge Lewis base impurities which are well known as catalyst poisons. Such poisoning was reported in the case of MAO-free cationic metallocene catalysts. The use of an [Al] scavenger concentration of similar order of magnitude led to a substantial increase in activity for the catalysts $Et(Ind)_2ZrMe$–$[Ph_3C][B(C_6F_5)_4]$–$AlMe_3$ or $Et(Ind)_2ZrCl_2$–$[Ph_3C][B(C_6F_5)_4]$–$AlEt_3$ [11,12]. On the other hand, one has to take into account that a low MAO concentration may not be sufficient to convert all metallocenes into active cationic metallocenes. When neutral metallocenes are present, complex formation between neutral and cationic metallocenes can reduce active site concentration even further, thus accounting for low catalyst activities. Moreover, since neutral metallocenes attached to polymer chains are still able to undergo chain termination via β-hydride elimination, this fast equilibrium of active cationic and dormant neutral metallocenes shifted towards dormant neutral metallocenes would explain lower molecular weights at low MAO concentrations.

3. Conclusions

The impact of MAO and propene concentration, both of which promote catalyst activity and poly(propene) molecular weight, when propene is polymerized on MAO-activated *rac*-Me_2Si(2-Me–Benz[e]Ind)$_2ZrCl_2$, provides experimental evidence for the presence of rapid equilibria between active cationic and coordinatively saturated dormant metallocene sites. At optimum [Al] concentration, most metallocenes are alkylated and converted into the active cationic metallocenes with weakly coordinating MAO-complexed counter-ions. At higher concentrations, excess MAO and olefin compete for vacant coordination sites. Therefore, in order to rank the performance of various metallocene-based Ziegler–Natta catalysts, in addition to the propene concentration and [Zr] concentration the total [Al] concentration should be listed instead of the [Al]/[Zr] molar ratio. This insight into the basic interaction of metallocenes and MAO activator may lead to novel metallocene catalysts where large portions of expensive MAO activators are replaced by economically more favourable cocatalysts.

4. Experimental details

The synthesis of the zirconocene *rac*-Me_2Si(2-Me–Benz[e]Ind)$_2ZrCl_2$ has been described previously [8]. The time dependence of the polymerization activity was determined by the pressure drop in a thermostated propene storage vessel when keeping the propene pressure constant in a thermostated 2 l Büchi-glass polymerization reactor as described previously [13]. All catalyst components were handled and stored under argon. Argon (purity, 99.99%; Messer Griesheim GmbH) was purified by passing it through BTS catalyst (BASF AG) and a 0.4 nm molecular sieve. Polymerization grade propene (BASF AG) was stored over $Al(^iBu)_3$–toluene prior to use. Toluene p.a. (Roth AG) was purified by passing through a column with acidic Al_2O_3 (Merck AG) and distillation over $LiAlH_4$ followed by at least 12 h refluxing over Na–K alloy and fresh distillation prior to use. The autoclave and pressure buret were washed with an approximately 1 wt% $Al(^iBu)_3$–toluene solution at 60 °C. The required amount (2.2 ml for $[Al] = 5$ mmol l^{-1}) of a 10 wt% solution of MAO in toluene (Witco AG; $M_a \approx 800$ g mol^{-1}) was added to 700 ml of toluene to obtain the desired MAO concentration. 600 ml of this solution were cannulated into the evacuated autoclave followed by saturation with propene at a total pressure of 2 bar at 40 °C. 30 ml of the above solution were used to dissolve 1.23 or 2.46 μmol of the zirconocene. 20 min later 15 ml of this solution were injected into the thermostated pressurized reactor via a pressure buret to start the reaction. The concentration was thus 1 or 2 μmol l^{-1} for the zirconocene. Temperature control was within ± 0.2 °C. The measured propene consumption is corrected for the change in propene solubility due to these temperature changes according to the known temperature dependence of propene solubility. The reaction was stopped by venting off the propene and precipitating the polymer in 1 l of methanol with 40 ml of 10% aqueous HCl and 0.5 g of 2,6-di-tet-butyl–4-methyl-phenol (BHT). After stirring the mixture over night the polymer was filtered off and washed with methanol and dried at 60 °C at reduced pressure to constant weight.

NMR spectra were recorded, using solutions of 60 mg of polymer in 0.5 ml of $C_2D_2Cl_4$ at 400 K, by means of a Bruker ARX 300. ^1H NMR spectra were recorded at 300 MHz with 128 scans and 6172.84 Hz spectra width and ^{13}C NMR spectra at 75.4 MHz with a 30° pulse angle, 3.5 s pulse repetition, 11 111.11 Hz spectra width and 4000 scans. Melting points were determined by differential scanning calorimetry from the melting endotherm at a heating rate of 20 K min^{-1} after previous heating to 185 °C and cooling to 50 °C at a 10 K min^{-1} cooling rate. The polymer molecular weight and molecular weight distribution were determined by size exclusion chromatography and viscosity measurements at the Polymer Research Division of BASF AG.

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