Dialkylzinc Compounds as Chain Transfer Agents in Ethylene and Propylene Polymerizations Catalyzed by Metallocene Catalysts

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Dialkylzinc compounds (ZnR_2) with the alkyl groups of different steric hindrance were used as chain transfer agents in ethylene and propylene polymerizations catalyzed by two conventional metallocene catalysts including *rac*-Et(Ind)$_2$ZrCl$_2$ and *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$. In general, catalyst activities for ethylene polymerizations are barely affected by chain transfer agents, regardless of the R type; however, there are significant activity reductions in propylene polymerizations when the R in ZnR_2 is less hindered, and as R becomes bulkier, catalyst activities are gradually restored. ZnR_2 and metallocene catalyst active site tend to form a reversible and catalytically inactive complex, thus the geometry congested ZnR_2 would reduce complex formation tendency and hence decreased its negative effect on catalyst activities.

Keywords: Dialkylzinc, chain transfer, olefin polymerization, metallocene catalyst (changed to *metallocene catalyst*)

1 Introduction

Chain transfer to dialkylzinc compounds, often referred to as zinc(Zn)-based chain transfer reaction (1–9), has recently raised renewed interest in olefin coordination polymerization, presumably because of the recent discovery of diethylzinc (ZnEt$_2$) as a reversible chain transfer agent causing a unique effect of chain shuttling between two distinctively different catalyst active sites, resulting in the preparation of multiblock, "blocky" poly(ethylene-co-1-octene) materials by virtue of differing capabilities for 1-alkene incorporation between the two active propagating centers, and these highly valued polyolefin materials are not accessible through the traditional methods (10–18). The driving force behind this scientific rebirth is certainly the rapid developing olefin coordination polymerization catalyst technologies, especially those of the well-defined single site catalysts (e.g. metallocene and non-metallocene catalysts) that

allow good understandings of the catalyst properties so as to manipulate polymerization process to accomplish specific goals. In fact, it was the ingenious combination of single site catalysts based on a bis(phenoxyimine)-based Group 4 complex (FI catalysts) (19–23) and a hafnium pyridylamide complex (24,25) to carry out the chain shuttling polymerization, which was based on the concept of the well-known "catalyzed chain growth" (26–28) and "coordinative chain-transfer" (29) reaction.

Reviewing the scarce literature on Zn-based chain transfer reaction, we have found that, as far as single site catalysts are concerned, it does not matter they are metallocene- or non-metallocene-type, the past reports are overwhelmed by ethylene, or ethylene-rich polymerization reaction. As for α-olefin polymerizations, only very recently Sita (30) reported the first example of living coordinative chain-transfer polymerization of propylene, in which atactic polypropylene was produced using Cp*HfMe$_2$[N(Et)C(Me)N(Et)]/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in the presence of varying amounts of ZnEt$_2$ as a chain transfer agent. Herein, we report the polymerization of ethylene and propylene in the presence of dialkylzinc compounds with the alkyl groups of different steric hindrance catalyzed by two conventional metallocene catalysts *rac*-Et(Ind)$_2$ZrCl$_2$ and *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$.

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Table 1. Polymerization of ethylene catalyzed by *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/ZnR$_2^a$

run	ZnR$_2$	Zn/Cat	yield/g	A/10^6 g PE·molZr^{-1}·h^{-1}	M$_v$/10^4
0	—	0	1.470	8.82	14.9
1	ZnEt$_2$	10	1.522	9.13	6.9
2	ZnEt$_2$	20	1.463	8.78	3.1
3	ZnEt$_2$	40	1.405	8.43	1.4
4	ZnEt$_2$	100	1.532	9.19	0.6
5	Zn^{i}Pr$_2$	10	1.169	7.01	11.1
6	Zn^{i}Pr$_2$	20	1.282	7.69	8.4
7	Zn^{i}Pr$_2$	40	1.061	6.37	6.1
8	Zn^{i}Pr$_2$	100	1.010	6.06	4.2
9	Zn^{t}Bu$_2$	10	1.212	7.27	14.4
10	Zn^{t}Bu$_2$	20	1.217	7.30	13.8
11	Zn^{t}Bu$_2$	40	1.122	6.73	13.3

^{a}Polymerization conditions: 40°C, 5 min, ethylene pressure = 1 atm; cat. 2μ; Al/Zr = 1000. toluene = 80 ml.

Table 2. Polymerization of propylene catalyzed by *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/ZnR$_2^a$

run	ZnR$_2$	Zn/Cat	yield/g	A/10^6 g PE·molZr^{-1}·h^{-1}	M$_v$/10^4
0	—	0	1.381	8.28	1.2
1	ZnEt$_2$	10	0.483	2.90	1.0
2	ZnEt$_2$	20	0.247	1.48	0.76
3	ZnEt$_2$	40	0.083	0.50	0.38
4	ZnEt$_2$	100	0.028	0.17	0.15
5	Zn^{i}Pr$_2$	10	0.655	3.93	0.96
6	Zn^{i}Pr$_2$	20	0.370	2.22	0.75
7	Zn^{i}Pr$_2$	40	0.207	1.24	0.51
8	Zn^{i}Pr$_2$	100	0.125	0.75	0.38
9	Zn^{t}Bu$_2$	10	0.851	5.11	1.1
10	Zn^{t}Bu$_2$	20	0.674	4.04	1.0
11	Zn^{t}Bu$_2$	40	0.481	2.89	0.98
12	Zn^{t}Bu$_2$	100	0.421	2.53	0.88

^{a}Polymerization conditions: 40°C, 5 min, propylene pressure = 1 atm; cat. 2μ; Al/Zr = 1000. toluene = 50 ml.

Table 3. Polymerization of ethylene catalyzed by *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$/MAO/ZnR$_2^a$

run	ZnR$_2$	Zn/Cat	yield/g	A/10^6 g PE·molZr^{-1}·h^{-1}	M$_v$/10^4
0	—	0	0.903	5.42	21.0
1	ZnEt$_2$	10	0.856	5.14	5.8
2	ZnEt$_2$	20	0.973	5.84	3.9
3	ZnEt$_2$	40	1.065	6.39	2.2
4	ZnEt$_2$	100	1.458	8.75	1.5
5	Zn^{i}Pr$_2$	10	1.177	7.06	12.3
6	Zn^{i}Pr$_2$	20	1.028	6.17	10.6
7	Zn^{i}Pr$_2$	40	0.952	5.71	8.4
8	Zn^{i}Pr$_2$	100	1.063	6.38	5.9
9	Zn^{t}Bu$_2$	10	1.039	6.23	16.4
10	Zn^{t}Bu$_2$	20	0.994	5.96	14.3
11	Zn^{t}Bu$_2$	40	1.143	6.86	12.2
12	Zn^{t}Bu$_2$	100	0.944	5.66	11.1

^{a}Polymerization conditions: 40°C, 5 min, ethylene pressure = 1 atm; cat. 2μ; Al/Zr = 1000. toluene = 80 ml.

Table 4. Polymerization of propylene catalyzed by *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$/MAO/ZnR$_2^a$

run	ZnR$_2$	Zn/Cat	yield/g	A/10^6 g PP·molZr^{-1}·h^{-1}	M$_v$/10^4
0	—	0	4.287	25.72	5.2
1	ZnEt$_2$	10	1.628	9.77	2.6
2	ZnEt$_2$	20	0.848	5.09	1.5
3	ZnEt$_2$	40	0.432	2.59	0.50
4	Zn^{i}Pr$_2$	10	1.162	6.97	3.3
5	Zn^{i}Pr$_2$	20	0.767	4.60	2.5
6	Zn^{i}Pr$_2$	40	0.357	2.14	1.0
7	Zn^{i}Pr$_2$	100	0.118	0.71	0.5
8	Zn^{t}Bu$_2$	10	1.796	10.78	5.1
9	Zn^{t}Bu$_2$	20	1.490	8.94	2.6
10	Zn^{t}Bu$_2$	40	0.749	4.49	1.5
11	Zn^{t}Bu$_2$	100	0.424	2.54	0.9

^{a}Polymerization conditions: 40°C, 5 min, propylene pressure = 1 atm; cat. 2 μ; Al/Zr = 1000. toluene = 50 ml.

2 Experimental

2.1 Materials and Instruments

All O$_2$- and moisture-sensitive manipulations were carried out inside an argon-filled vacuum atmosphere dry-box equipped with a dry train. ZnCl$_2$ was dried by refluxing in SOCl$_2$ for 24 h. ZnEt$_2$ (1.5 M solution in toluene) was purchased from J&K Chemical Ltd. Toluene (Sinopharm Chemical Reagent Beijing Co., Ltd. of China) was distilled over sodium and benzophenone under nitrogen before use. Methylaluminoxane (MAO) (1.4 M in toluene) and *rac*-Et(Ind)$_2$ZrCl$_2$ were kindly supplied by CNPC Lanzhou Chemical Company. *Rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$ was prepared according to the procedures described in ref. (31). MAO was depleted of free trimethylaluminum (TMA) by drying in vacuum to a free-flowing powder, and then dissolved in toluene before use. Polymerization grade ethylene and propylene were supplied by Yanshan Petrochemical Co. of China.

Room temperature ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AVANCE 400 instrument. High temperature ^{1}H and ^{13}C-NMR spectra were carried out in 1,2,4-trichlorobenzene at 390 K using a Bruker DMX 300 spectrometer. The viscosity-average molecular weight (M$_v$) of polyethylene and polypropylene was calculated according to the equation of $[\eta] = 2.30 \times 10^{-4}M_v^{0.82}$ and $[\eta] = 1.58 \times 10^{-4}M_v^{0.77}$, respectively (32) and the intrinsic viscosity of the polymers was measured in decahydronaphthalene at 135 ± 0.1°C.

2.2 Synthesis of Zn^{i}Pr$_2$ and Zn^{t}Bu$_2$

Both Zn^{i}Pr$_2$ and Zn^{t}Bu$_2$ were prepared from Grignard agents and anhydrous ZnCl$_2$ (33). Zn^{i}Pr$_2$ ^{1}H-NMR (400 MHz, CDCl$_3$, solvent reference at 7.26 ppm): δ 0.70–0.74 (m, Me$_2$CH-), 1.19–1.20 (d, (CH$_3$)$_2$). Zn^{t}Bu$_2$ ^{1}H-NMR
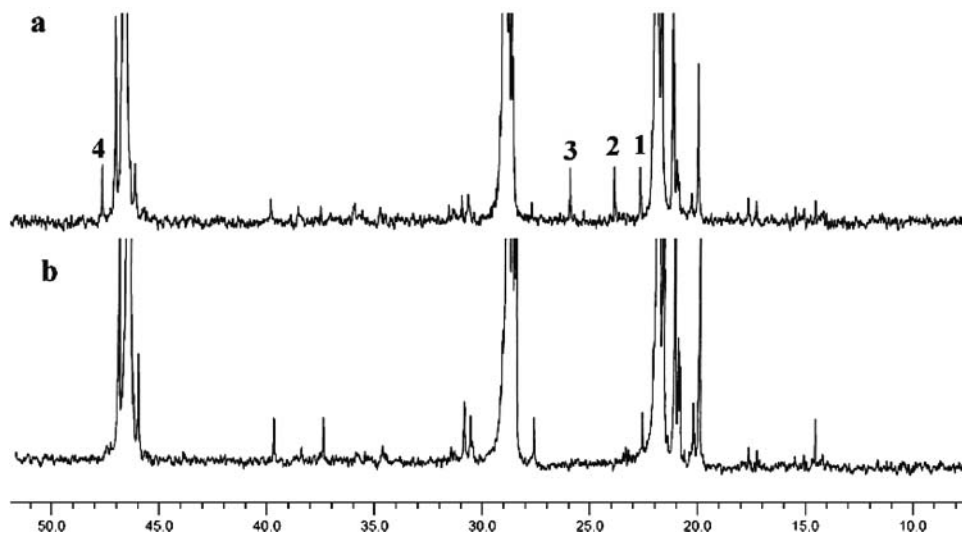
Fig. 1. ^{13}C-NMR of polypropylene prepared from *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/Zn^{t}Bu$_2$. (a) Zn/Zr = 100 ; (b) Zn/Zr = 0.

(400 MHz, CDCl$_3$, solvent reference at 7.26 ppm):δ 1.05 (s, (CH$_3$)$_3$).

2.3 Polymerization

Polymerization was carried out under atmospheric pressure in toluene in a 250 mL glass reactor equipped with a magnetic stirrer. Toluene (50 mL) was introduced into the ethylene (or propylene) purged reactor and stirred vigorously (600 rpm). The toluene was kept at 40°C and then MAO in toluene was injected. After stirring for 5 min, a prescribed amount of dialkylzinc in toluene was added and stirred for another 5 min. Then the polymerization was initiated by the addition of a toluene solution of the prescribed catalyst. After 5 min, acidic ethanol was added to terminate the polymerization. The precipitated polymer was isolated and dried at 50°C for 12 h in a vacuum oven.

3 Results and Discussion

In this paper, with two conventional metallocene catalysts, *rac*-Et(Ind)$_2$ZrCl$_2$ and *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$, in combination with MAO, we report a comparative study of Zn-based chain transfer reactions in both ethylene and propylene polymerizations, using dialkylzinc compounds as chain transfer agents. Our objective is to shed light into the field of Zn-based chain transfer reaction in a single site catalyst-based α-olefin polymerization system, which is to be extensively explored in the near future.

Firstly, we investigated ethylene polymerizations catalyzed by *rac*-Et(Ind)$_2$ZrCl$_2$ with a series of alkyl zinc compounds of different steric hindrance as chain transfer agents. The polymerization results are summarized in Table 1.

Increasing the amounts of ZnR$_2$, the molecular weight of polyethylene decreased with all the dialkylzinc compounds
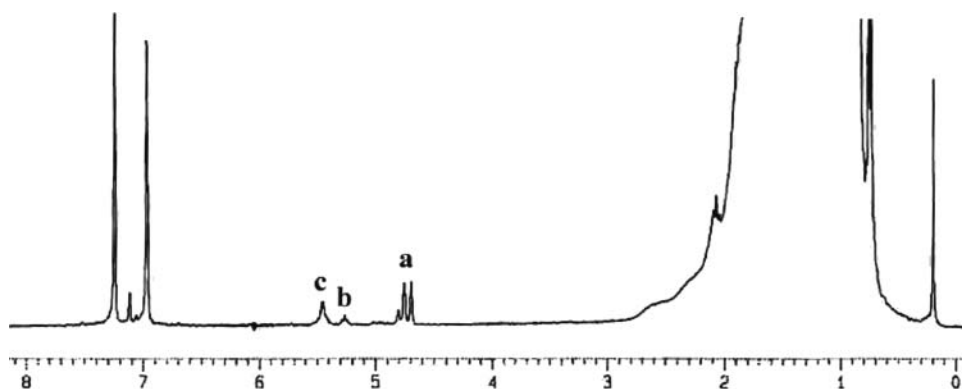
Fig. 2. ^{1}H-NMR of polypropylene prepared from *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/Zn^{t}Bu$_2$ at Zn/Zr = 100. (a) vinylidene; (b) CH$_3$CH$_2$CH$_2$CH-C(CH$_3$)P; (c) 2-butenyl. The corresponding olefin structures are assigned as previously described in literature (34).
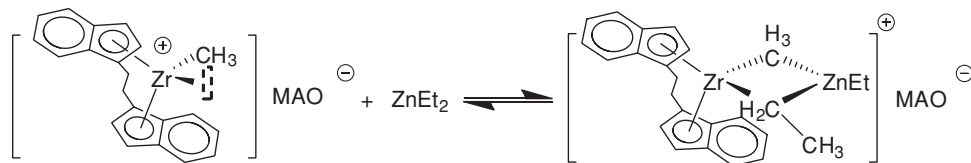
Sch. 1. Formation of Zr-Zn complex between Zr active sites and $ZnEt_2$ in *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/ZnEt$_2$ system.

studied. The molecular weight increased while increasing the size of the R group of dialkylzinc compounds. Obviously, the more congested the alkyl group, the slower the chain transfer rate of dialkylzinc will be. Therefore, the molecular weight of polyethylene prepared is lower for $ZnEt_2$ than that for Zn^tBu_2 under the same Zn/Zr. Comparable activities were obtained in the presence and in the absence of ZnR_2, which is in accordance with Gibson's results (28) catalyzed by bis(imino)pyridineiron catalyst. However, in the presence of dialkylzinc compounds, activities of propylene polymerization decreased greatly (Table 2).

Generally, dialkylzinc compounds are considered to be chain transfer agents in olefin polymerization and they are not supposed to affect polymerization activities greatly, which is what we observed in ethylene polymerization. But for propylene polymerization, it seems not to be the case. Increasing amounts of dialkylzinc compounds lead to a great reduction of propylene polymerization activities. Then, we studied ethylene and propylene polymerization catalyzed by another conventional metallocene catalyst *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$ and found the similar results (Table 3 and Table 4).

Dialkylzinc can coordinate with olefin polymerization catalytic active sites to form a bimetallic M-Zn complex (27) (Scheme 1). Due to its steric hindrance, the coordination ability of propylene is weaker than ethylene. For ethylene polymerization, monomer insertion is easier and faster than the complex of ZnR_2 with the active sites, namely, this equilibrium is shifted to the left when we adding ethylene into this catalytic system. Therefore, activities of ethylene polymerization were barely influenced by ZnR_2. But due to the weaker coordination ability of propylene monomer (it must be weaker than ZnR_2), when propylene monomer was introduced to this catalytic system, the equilibrium was hardly affected and most of the active sites would coordinate with $ZnEt_2$, and hence activities of propylene polymerization decreased.

In Tables 2 and 4, we also found that there is an increasing trend of activities of propylene polymerization while increasing the bulkiness of R group in ZnR_2. It was because when more congested dialkylzinc compound was introduced into this system, the complex formed between active sites and ZnR_2 became more unstable and the equilibrium would shift to the left easily when propylene was added (Scheme 1). Consequently, propylene polymerization activities increased. At the same time, a distinct manifestation of the polymerization product is an increase of polypropylene

molecular weight with the increasing steric hindrance of ZnR_2, which is consistent with Gibson's results in late-transition metal catalyzed ethylene polymerization (27).

There is another way to solve the low activity problems associated with Zn-based chain transfer reaction in metallocene-catalyzed propylene polymerization- to reduce the steric hindrance of metallocene catalyst (actually, this is what Sita (30) did), which made it easier for the insertion of propylene monomer into the active sites.

Gibson considered Zn^tBu_2 to be too bulky to interfere with the polymerization reaction catalyzed by bis(imino)pyridineiron catalyst (27). In our polymerization results, ^{13}C-NMR (Figure 1) of polypropylene prepared from *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/Zn^tBu_2 (a) presented the peaks at 22.63 (1), 23.83 (2), 25.89 (3) and 47.61 (4) ppm-typical chemical shifts of isobutyl group, which comes from hydrolysis of a metal-ended polymer chain or β-methyl transfer. We used dried MAO depleted of free TMA, and hence, chain transfer to aluminum must be in a very low level, which was what we saw in the spectrum of polypropylene prepared without Zn^tBu_2 (b) (no isobutyl peaks). In the ^{1}H-NMR (Figure 2) of polypropylene prepared at Zn/Zr = 100, there is no peaks of ally from β-methyl transfer either. As a result, the isobutyl group must be from Zn-terminated polymer chains upon hydrolytic workup, in other words, chain transfer to Zn^tBu_2 actually occurred in *rac*-Et(Ind)$_2$ZrCl$_2$ catalyzed propylene polymerization.

4 Conclusions

In conclusion, we investigate ethylene and propylene polymerizations catalyzed by two conventional metallocene catalyst including *rac*-Et(Ind)$_2$ZrCl$_2$ and *rac*-Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$ in the presence of a series of alkyl zinc reagents with the alkyl groups (R) of different steric hindrance as chain transfer agents. It is found that, in general, catalyst activities for ethylene polymerization are hardly affected by ZnR_2 the chain transfer agent, regardless of the R type; however, there are significant activity reductions in propylene polymerizations when the R in ZnR_2 is less hindered, and as R becomes bulkier, catalyst activities are gradually restored. These polymerization behaviors are explained by knowing the fact that ZnR_2 and metallocene catalyst active site tend to form a reversible, catalytically inactive complex and thus enlarged bulkiness of ZnR_2 reducing

complex formation tendency and decreasing its negative effect on catalyst activity.

Acknowledgement

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