INFLUENCE OF DIETHYLZINC ON THE ETHYLENE POLYMERIZATION CATALYZED BY α-DIIMINE NICKEL(II) COMPLEXES

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Abstract

The use of diethylzinc in the ethylene polymerization in addition to α-diimine nickel(II) bromide complexes activated by Et_2AlCl leads to an increase in the catalytic activity and branching density of resulting polyethylene. It was demonstrated that the effect of diethylzinc strongly depends on the ligand steric hindrances, leading to the formation of hyperbranched polyethylene with high melting temperature and crystallinity degree.

Key words: hyperbranched polyethylene, nickel, diethylzinc.
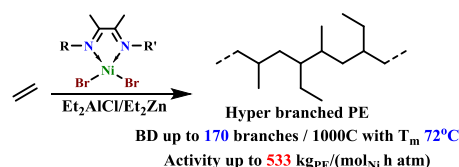
Introduction

Nickel(II) complexes have long been recognized as the catalysts for the direct production of branched and hyperbranched polyethylene (PE) from ethylene. Through the "chain-walking" mechanism, polyethylenes with varying branching degrees can be synthesized by tuning the ligand environment and reaction conditions. This method differs fundamentally from the conventional radical polymerization used for the synthesis of low-density polyethylene (LDPE) or the copolymerization of ethylene with expensive comonomers required for linear low-density polyethylene (LLDPE) [1, 2].

The ability to control the branching degree of polyethylene by adding different amounts of diethylzinc (DEZ) to the catalytic system based on α-diimine Ni(II) complexes **A** [3] and **B** [4–6] (Fig. 1) attracted our attention since this approach could be the key to creating highly branched polyethylenes directly from ethylene under controlled conditions.
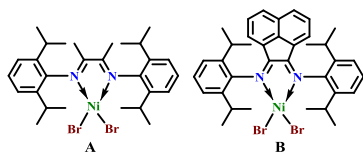

Figure 1. α-Diimine Ni(II) complexes **A** and **B**.

While previous studies have extensively examined the Brookhart-type nickel catalysts, the role of DEZ in fine-tuning the polymer microstructure remains largely unexplored. Our findings demonstrate that DEZ not only affects the polymerization activity but also provides a new strategy for achieving highly branched polyethylenes directly from ethylene under controlled conditions. To gain deeper insights into this effect, we systematically investigated the effect of DEZ as an additive in these well-established catalytic systems [7].

Results and discussion

In this work, we utilized the catalytic system based on α-diimine nickel(II) complexes **1**–**3** (Fig. 2) activated by 150 equiv. of Et_2AlCl (DEAC) in the presence or absence of $ZnEt_2$. Typically, the ethylene polymerization tests were performed under 3 atm of ethylene at 30 °C in chlorobenzene for 30 min, unless otherwise noted, and the results of this screening are presented in Table 1. We used chlorobenzene as a solvent instead of toluene to eliminate the side process of the Friedel–Crafts alkylation.
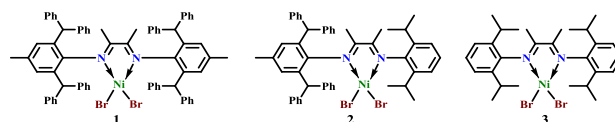

Figure 2. α-Diimine Ni(II) complexes **1**–**3**.

A series of nickel bromide complexes (**1**–**3**) with bulky α-diimine ligands was selected as the research objects since these complexes allow for examining the effect of steric hindrances around the catalytic center on the properties of the resulting polymer. As is shown in Table 1, upon activation of complexes **1**–**3** with 150 equiv. of DEAC (runs 1, 8, and 10), a decrease in the steric bulk leads to an increase in the catalytic activity of the system (125, 373, and 433 kg PE·mol(Ni)$^{-1}$·h^{-1}·atm^{-1}) owing to the easier access of ethylene molecules to the active center. However, this also facilitates the chain termination *via β*-elimination, resulting in a decrease of the molar mass from 271 to 172 kg/mol and an increase in the polydispersity index from 1.8 to 3.0 (runs 1 and 8). The reduced steric hindrances further promote the increased chain-walking activity of nickel, as is evidenced by the growing number of branches (44, 80, and 93 per 1000 carbons in runs 1, 8 and 10, respectively). An increase in the temperature from 30 to 60 °C also leads to the formation

Table 1. Ethylene polymerization catalyzed by complexes **1–3** in the presence or absence of ZnEt$_2$[a]

Run	Precatalyst	ZnEt$_2$, equiv.	Product, g	Activity[b]	M_n, kg/mol[c]	M_w, kg/mol[c]	PDI[c]	BD[d]	T_m, °C[e]	X_c, %[f]
1	**1**		0.75	125	271	474	1.8	44	72	14
2[g]	**1**		1.20	200	–	–	–	53	54	16
3	**1**	75	0.98	163	–	–	–	170	72	13
4	**1**	150	0.70	117	204	408	2.0	79	74	15
5[g]	**1**	150	1.40	233	–	–	–	93	56	16
6	**1**	300	0.75	125	–	–	–	107	74	17
7	**1**	600	0.90	150	–	–	–	104	73	18
8	**2**[h]		2.80	373	172	517	3.0	80	20	9
9	**2**[h]	150	3.40	453	100	280	2.8	92	10	7
10	**3**[h]		3.25	433	–	–	–	93	–2	11
11	**3**[h]	150	4.00	533	–	–	–	112	39	1

[a] general conditions: 4 μmol of the precatalyst, 3 atm of ethylene, 30 min, 30 °C, 50 mL of chlorobenzene, 150 equiv. of DEAC; [b] kg PE·mol(Ni)$^{-1}$·h^{-1}·atm^{-1}; [c] determined by GPC; [d] branching density, given per 1000 carbon atoms; [e,f] determined by DSC; [g] 60 °C ; [h] 5 μmol of the precatalyst.

of a more highly branched polymer with a lower melting temperature. These observations are in good agreement with the previous data obtained for these complexes activated by methylaluminoxane (MAO) in toluene [4].

To study the effect of the diethylzinc amount on the properties of the catalytic system, the most sterically hindered complex—compound **1**—was selected. The results of runs 3, 4, 6, and 7, using 75, 150, 300, and 600 equiv. of DEZ show a nonlinear relationship between the properties of the catalytic system and the amount of diethylzinc. The maximum activity was observed at 75 equiv. of DEZ; at 150 equiv., it dropped sharply and then gradually increased with further additions. The number of branches also showed a dip at 150 equiv., but despite this, an increase of 85% in the branching density was achieved relative to the system without diethylzinc. The tests with precatalysts **2** and **3** showed that even with the least favorable diethylzinc amount it is possible to reach a 15–20% increase in the branching degree of the resulting polyethylene and a 20% increase in the catalytic activity.

It is important to note that an increase in the branching degree due to the addition of diethylzinc to the catalytic system based on complex **1** has virtually no effect on the crystallinity (13–17%) and melting temperature (72–74 °C) of the resulting PEs. This result cannot be achieved by using temperature adjustments to increase the branching density or by employing less sterically hindered catalysts.

We believe that a strong effect of diethylzinc on the degree of branching is likely due to the possibility of reversible ligand exchange between the active nickel center and diethylzinc, resulting in the formation of an α-diimine zinc complex (Scheme 1), described in the literature [8]. This process exposes the nickel site, enabling it to perform chain walking much more actively. This effect is most pronounced with highly sterically hindered ligands, where a significant steric tension exists bet-

ween the ligand and the polymer chain on the metal, shifting the equilibrium towards the zinc complex. Furthermore, such a pronounced increase in the branching density was not observed by other researchers [4] presumably since they used less polar toluene as a solvent for the ethylene polymerization, in which the naked nickel-polymer cation is not enough stable.

Conclusions

The addition of diethylzinc to the ethylene polymerization reaction using the catalytic systems based on α-diimine nickel complexes activated by DEAC in a polar chlorobenzene medium can significantly increase the branching density of the resulting PEs by up to 3.4 times for complex **1**, with an activity increase of up to 30% for the same complex.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, steric maps, NMR spectra, GPC and DSC data. For ESI, see DOI: 10.32931/io2537a.

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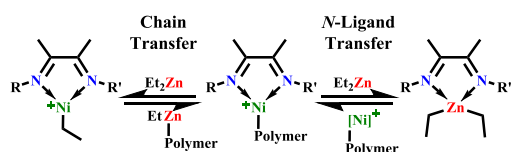
Scheme 1. Two possible pathways of the interaction of ZnEt$_2$ with the nickel catalytic site.

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