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ORIGINAL PAPER

# Monomer effect on the chain transfer by diethyl zinc in olefin polymerization by metallocene catalysts

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## ABSTRACT

The present paper systematically studies the homo- and copolymerization of ethylene or propylene using metallocene as catalyst and diethyl zinc as chain transfer agent to obtain the polyolefin waxes with narrow molecular weight distribution and with a high activity. The molecular weight of the resultant polymer could be controllable by the concentration of diethyl zinc quantitatively. The introduction of α-olefin into the ethylene polymerization system would shield the chain transfer action, and the shielding effect in propylene (co) polymerization is more serious, due to the mass transfer resistance of the substituents on the monomers. Branched comonomer and long chain comonomer provide stronger shielding effect. The regression results show that the order of the chain transfer reaction of propylene polymerization is smaller than that of ethylene polymerization, and the order of the chain transfer reaction of copolymerization is less than that of homopolymerization. It indicates that the substituent on the monomer would result in the deviation of the regression data from the ideal primary reaction order. **Polyolefins J (2021) 8: 85-91**

**Keywords:** Metallocene catalysts; olefin polymerization; chain transfer; diethyl zinc; molecular weight.

## INTRODUCTION

Polyolefin is the most important synthetic polymer material in daily life. In recent years, polyolefin materials with new functions and high added value have gradually attracted the attention of researchers [1-3]. Polyolefin with low molecular weight less than 10,000 could be used as wax (polyolefin wax, PO wax). In plastic processing, polyolefin wax can be used as a lubricant, brightener and dispersant for color masterbatch. PO wax can also be used as a carrier of pigments to improve the abrasion resistance and dispersibility of paints and inks, so that the products have good gloss and three-dimensional effect. Used in wax products such as floor wax and car wax, PO wax can increase the softening point of wax products, increase strength and surface gloss. In a word, PO wax plays a role of lubrication and dispersion in various applications, and

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can improve the look and feel of products at the same time. PO wax was obtained through cracking the high molecular weight olefin polymer into a low molecular weight polymer, extracting the low molecular weight part in the process of olefin polymerization, or direct olefin polymerization. The molecular weight distribution (MWD) of PO wax obtained by the first two methods and the polymerization by Ziegler-Natta catalyst is relatively broad. Olefin polymerization based on metallocene catalyst offers an opportunity to produce the PO wax with uniform and controllable molecular weight distribution and chemical composition distribution. Compared with traditional PO wax, metallocene product has better properties and can be used as dye dispersant, lubricant, compatibilizer and processing additives. The usual way to reduce the molecular weight of polyolefin is to add hydrogen during polymerization. However, under the condition of high hydrogen concentration, whether using Ziegler-Natta catalyst or metallocene catalyst, the polymerization activity will be reduced and the molecular weight distribution of the polymer will be broadened [4]. This not only decreases the production efficiency, but also reduces the product quality. Therefore, finding an effective chain transfer agent for olefin polymerization instead of hydrogen is particularly critical for the efficient production of high-quality PO wax [5-11].

Some organic metal compounds can be used as chain transfer agents for olefin polymerization, such as aluminum [12-14], magnesium [15-17] and zinc [18-25]. In particular, alkyl zinc can not only reduce the molecular weight of polyolefin, but also play the role of chain shuttle agent to synthesize olefin block copolymers [26]. We previously reported that the activity of ethylene homo- and copolymerization can be greatly improved, when a small amount of diethyl zinc (DEZ) was added to the metallocene-MAO polymerization system [27]. We inferred the newly generated mixed alkylaluminoxane by the alkyl exchanging reaction between DEZ and MAO that may have a better co-catalytic effect. We also reported that the use of the appropriate amount of DEZ in metallocene catalytic system can effectively adjust the molecular weight of polyethylene and found the quantitative relationship between the concentration of DEZ and the molecular weight of polyethylene [28].

Considering the diversity of PO wax market, in this study, we use this method to realize the accurate control of the molecular weight of ethylene/α-olefin copolymer and homopolymer and copolymer of propylene. And we found that the substituent on monomer could strongly influence the chain transfer action of DEZ.

## EXPERIMENTAL

### General Procedure

All experiments were carried out under a nitrogen atmosphere in a vacuum atmosphere drybox or using standard Schlenk techniques, unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Toluene was distilled in the presence of sodium and benzophenone under a nitrogen atmosphere, and was stored in a Schlenk tube in the drybox over molecular sieves. Diethyl zinc (DEZ) solution in toluene (1.5 M) was purchased from Acros (Belgium), and a solution of 0.2 mmol/mL toluene was prepared before use. Metallocene catalysts, **1** *rac*-$(CH_2)_2Ind_2ZrCl_2$(99%), **2** (1-Me-3-$^n$BuCp)$_2ZrCl_2$(99%), **3** *rac*-$Me_2SiInd_2ZrCl_2$(99%), and **4** *rac*-$Me_2Si$(2-Me-4-Ph-Ind)$_2ZrCl_2$(99%) were obtained from APAC Pharmaceutical. MAO (methylaluminoxane) solution in toluene (10 wt%) was purchased from Albemarle. 1-Hexene (hex, 99%), 4-methyl-1-pentene (MP, 98+%), and 1-octadecene (otd, 98%) were procured from TCI, and were used as received.

### Polymerization

Polymerization was conducted in toluene in a 250 mL glass reactor with an oil bath. The glass reactor was purged with vacuum and nitrogen, and finally in an ethylene or propylene atmosphere. For example, run 8 in Table 1, keeping the oil bath at 70°C, toluene (26.2 mL), 1-hexene (0.3 mL), MAO toluene solution (1.5 mL, 2.5 mmol), and diethyl zinc solution in toluene (1mL, 0.2mmol) were introduced into the reactor in this order. Then *rac*-$(CH_2)_2(Ind)_2ZrCl_2$ solution in toluene (1 mL, 1.0 μmol) was injected to start the polymerization. The mixture was stirred magnetically for 20 min. Subsequently, the mixture was poured into ethanol containing concentrated hydrochloric acid and

**Table 1**. Ethylene (co)polymerization in the presence of DEZ[a].

| Run | Cat | Comonomer[b] (mmol) | Zn/Zr[c] (molar ratio) | Polymer (g) | Activity (kg-P/ mol-cat/hr) | $M_n$[d] | PDI[d] |
|---|---|---|---|---|---|---|---|
| **1**[e] | 1 | 0 | 0 | 1.22 | 3660 | 22216 | 3.07 |
| **2**[e] | 1 | 0 | 200 | 1.33 | 3990 | 3946 | 2.23 |
| **3**[e] | 1 | 0 | 400 | 1.21 | 3630 | 1778 | 2.06 |
| **4**[e] | 1 | 0 | 600 | 1.25 | 3750 | 1179 | 1.91 |
| **5**[e] | 1 | 0 | 800 | 1.11 | 3330 | 849 | 1.84 |
| **6**[e] | 1 | 0 | 1000 | 0.73 | 2190 | 630 | 1.66 |
| **7** | 1 | Hex, 2.42 | 0 | 1.53 | 4590 | 30000 | 2.16 |
| **8** | 1 | Hex, 2.42 | 200 | 1.40 | 4200 | 4037 | 2.26 |
| **9** | 1 | Hex, 2.42 | 400 | 1.24 | 3720 | 2068 | 2.11 |
| **10** | 1 | Hex, 2.42 | 600 | 1.11 | 3330 | 1373 | 1.90 |
| **11** | 1 | Hex, 2.42 | 800 | 1.09 | 3270 | 1090 | 1.87 |
| **12** | 1 | Hex, 2.42 | 1000 | 1.10 | 3300 | 1073 | 1.64 |
| **13** | 1 | MP, 3.16 | 400 | 0.34 | 1020 | 1335 | 2.20 |
| **14** | 1 | MP, 3.16 | 800 | 0.69 | 2070 | 819 | 1.99 |
| **15** | 1 | otd, 2.49 | 400 | 1.13 | 3390 | 1011 | 3.73 |
| **16** | 1 | otd, 2.49 | 800 | 1.23 | 3690 | 896 | 2.40 |
| **17** | 2 | hex, 2.42 | 0 | 1.34 | 4020 | 3545 | 2.73 |
| **18** | 2 | hex, 2.42 | 200 | 0.59 | 1770 | 2296 | 2.31 |
| **19** | 2 | hex, 2.42 | 400 | 0.50 | 1500 | 931 | 2.24 |
| **20** | 2 | hex, 2.42 | 600 | 0.46 | 1380 | 681 | 2.06 |
| **21** | 2 | hex, 2.42 | 800 | 0.39 | 1170 | 571 | 1.85 |
| **22** | 2 | hex, 2.42 | 1000 | 0.31 | 930 | 515 | 1.79 |
| **23** | 3 | hex, 2.42 | 0 | 0.61 | 1830 | 41454 | 2.37 |
| **24** | 3 | hex, 2.42 | 200 | 0.39 | 1170 | 2811 | 2.14 |
| **25** | 3 | hex, 2.42 | 400 | 0.23 | 690 | 1255 | 1.96 |
| **26** | 3 | hex, 2.42 | 600 | 0.15 | 450 | 789 | 1.76 |

[a] Conditions: cat **1**, *rac*-$(CH_2)_2Ind_2ZrCl_2$; **2**, (1-Me-3-$^n$BuCp)$_2ZrCl_2$; **3**, *rac*-$Me_2SiInd_2ZrCl_2$: 1 mmol, MAO 2.5 mmol (Al/Zr=2500), ethylene 1 atm, 80°C, 20 min, in toluene, total volume 30 mL; [b] comonomer: hex (1-hexene), MP (4-methyl-1-pentene), otd (1-octadecene); [c] molar ratio of DEZ to catalyst; [d] determined by GPC; [e] results of runs 1 to 6 are extracted from reference [28].

stirred for 6 h. The resultant polymer was gathered on a filter paper by filtration, and washed thoroughly with EtOH. After drying in vacuo under 60°C for 24 h, 1.40 g of the polymer was obtained.

**Polymer Characterization**

The molecular weight was determined by using gel permeation chromatography (GPC, polystyrene calibration) on a Waters Alliance GPC V2000 at 150°C with 1,2,4-trichlorobenzene as the eluent, and the infrared (IR) as the detector.

## RESULTS AND DISCUSSION

Four metallocene catalysts **1**, *rac*-$(CH_2)_2Ind_2ZrCl_2$; **2**, (1-Me-3-$^n$BuCp)$_2ZrCl_2$; **3**, *rac*-$Me_2SiInd_2ZrCl_2$; and **4**, *rac*-$(CH_3)_2Si$(2-Me-4-Ph-Ind)$_2ZrCl_2$) were used for ethylene (co)polymerization and propylene (co) polymerization in the presence of DEZ, and the results are summarized in Tables 1 and 2. The results showed that DEZ could effectively reduce the molecular weight of homopolymer or copolymer, and the molecular weight distribution became narrower with the increase of Zn/Zr.

For both ethylene and propylene, the molecular weight of the copolymer with 1-hexene was higher than that of homopolymer in the absence of DEZ (run 7 vs run 1 and run 33 vs run 27). The observation may mean that the chain transfer reaction in the polymerization system is inhibited by the comonomer. The comonomer has larger substituents than ethylene or propylene, and thus has greater steric resistance, which may hinder the mass transfer process of chain transfer, thereby reducing the chain transfer efficiency and leading to the increase of the polymer molecular weight. When DEZ was added to the polymerization system as a chain transfer agent, the molecular weight of the polymer produced by all systems decreased with the increase of DEZ feeding (see Figure 1). The molecular weight of ethylene copolymer was higher than that of homopolymer, but the molecular weight of propylene copo-

**Table 2**. Propylene (co)polymerization in the presence of DEZ[(a)].

| Run | 1-hexene (mmol) | Zn/Zr (molar ratio) | Polymer (g) | Activity (kg-P/mol-cat/hr) | Mn[(b)] | PDI[(b)] |
|---|---|---|---|---|---|---|
| **27** | - | 0 | 4.95 | 7430 | 3127 | 3.50 |
| **28** | - | 50 | 3.78 | 5670 | 2064 | 2..65 |
| **29** | - | 100 | 3.08 | 4620 | 1713 | 2.51 |
| **30** | - | 150 | 2.70 | 4050 | 1454 | 2.23 |
| **31** | - | 200 | 2.07 | 3110 | 1186 | 2.24 |
| **32** | - | 250 | 2.31 | 3470 | 1087 | 2.34 |
| **33** | 2.42 | 0 | 2.42 | 3630 | 7383 | 2.76 |
| **34** | 2.42 | 50 | 2.70 | 4050 | 1969 | 2.27 |
| **35** | 2.42 | 100 | 2.34 | 3510 | 1512 | 2.49 |
| **36** | 2.42 | 150 | 1.02 | 1530 | 1354 | 1.800 |
| **37** | 2.42 | 200 | 1.12 | 1680 | 1116 | 1.99 |

[(a)] Conditions: cat **4**, *rac*-$(CH_3)_2Si$(2-Me-4-Ph-Ind)$_2ZrCl_2$ 2 mmol, MAO 2.5 mmol, propylene 1 atm, 70°C, 20 min, in toluene, total volume 30 mL; [(b)] determined by GPC.

lymer is close to or even lower than that of homopolymer. Although the molecular weight of copolymer is slightly different from that of the corresponding homopolymer under the same conditions, the trend of molecular weight change is the same with the increase of DEZ amount, may indicating that the chain transfer mechanism of copolymerization and homopolymerization is the same.

There should be several types of chain transfer reactions (such as transfer to MAO) in a polymerization system without DEZ. But the introduction of comonomers effectively shielded one or more types of chain transfer reaction, so copolymerization without DEZ resulted in the higher molecular weight polymers. However, the chain transfer ability of DEZ is much stronger than that of other chain transfer agents. Adding a small amount of DEZ, shielding brought by comonomers was broken, then the same decreasing trend of molecular weight as homopolymerization was observed.

In addition, 4-methyl-1-pentene and 1-octadecene were used as comonomers for ethylene copolymerization to further explore the effect of comonomers on chain transfer reaction (see Table 1). When the Zn/Zr changed from 400 to 800, comonomer with different structure exhibited the different response of the molecular weight decline of polymers (see Figure 2). The molecular weight of 4-methyl-1-pentene copolymer at 800 of Zn/Zr ratio is 61% of that of 400, and the value for 1-octadecene is 89%. This means that DEZ plays a much smaller role in 1-octadecene polymerization than it does in 4-methyl-1-pentene polymerization. To compare with ethylene homopolymerization and ethylene/1-hexene copolymerization, we can get the order of molecular weight decline as fol-

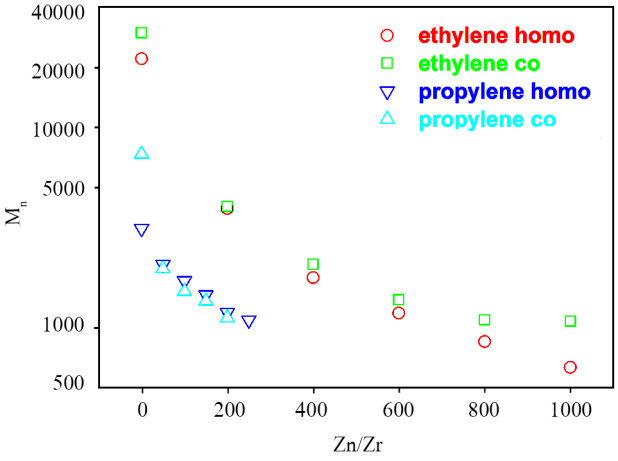



**Figure 1**. Comparison of the effect of DEZ on molecular weight of ethylene (by cat 1) or propylene (by cat 4) homo- and copolymer.

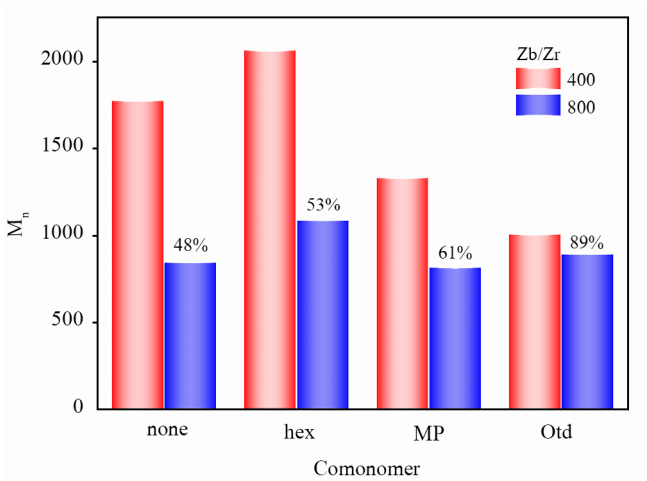



**Figure 2**. Comparison of the chain transfer effect of ethylene copolymerization by using different comonomers.

lows: homopolymerization (48%) > 1-hexene (53%) > 4-methyl-1-pentene (61%) > 1-octadecene (89%). Although 1-hexene and 4-methyl-1-pentene have the same number of carbon atoms, it is expected to provide greater steric resistance due to the branched structure of the latter. These phenomena indicated that the comonomer with greater steric hindrance reduced the probability of the chain transfer reaction. The effects of 1-hexene on DEZ chain transfer in ethylene polymerization under different Zn/Zr ratios were further considered. In order to compare the effect of the amount of DEZ on the molecular weight change of the polymer, the molecular weight of the ethylene homopolymer obtained when the Zn/Zr ratio is 200 is set to 100%, and the percentage of the molecular weight of the polymer at a higher Zn/Zr ratio can be calculated. Ethylene copolymers do the same. This change is shown in Figure 3. It can be seen that in all Zn/Zr ratios, the change rate of copolymer molecular weight is less than that of homopolymer molecular weight, indicating that the introduction of comonomer weakens the chain transfer effect of DEZ. However, when the similar method was used for analysis propylene polymerization (see Figure 4), the results seem to contradict those of ethylene polymerization. This may be because propylene and higher α-olefins may themselves play as a better role in chain transfer. At the same time, in propylene polymerization, as the main monomer, the higher concentration of propylene will also shield the chain transfer of DEZ. Thus, the chain transfer effect and shielding against DEZ of propylene

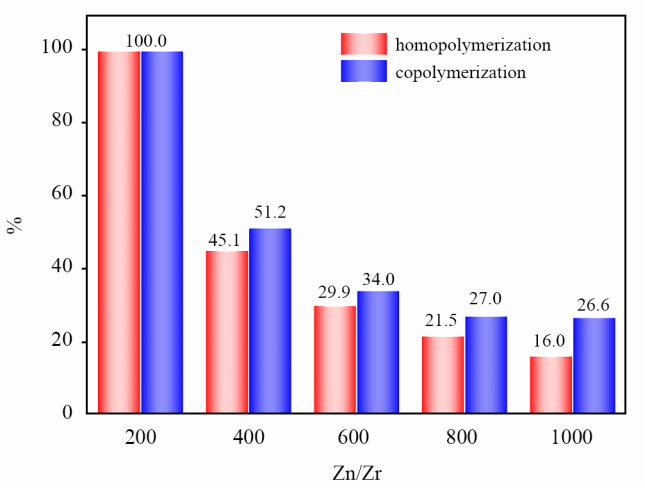



**Figure 3**. Comparison of the decline percent of molecular weight of ethylene (co)polymer.

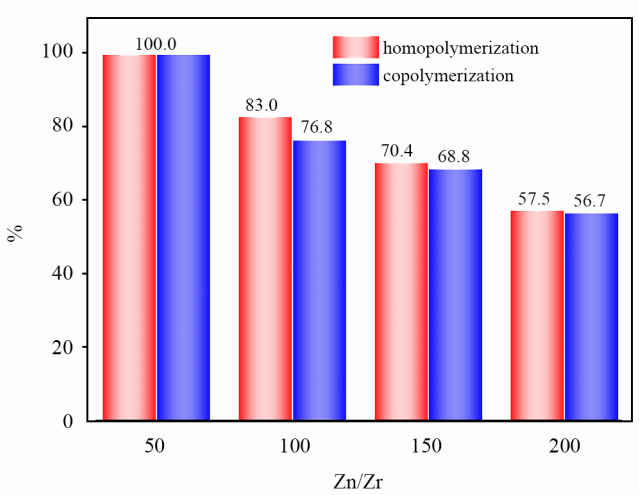



**Figure 4**. Comparison of the decline percent of molecular weight of propylene (co)polymer.

and higher α-olefins play the roles at the same time. In other words, monomers, including propylene and higher α-olefins, reduced the molecular weight of the polymer by direct chain transfer and prevented the reduction by shielding DEZ chain transfer.

In the previous work [28], we got the relationship between the molecular weight of polyethylene and DEZ concentration, based on the mechanism of chain transfer to hydrogen [2], as the following equation:

$$\ln\left(\frac{\bar{M}_n^o}{\bar{M}_n^z}-1\right)=\ln k+n\ln[DEZ] \qquad (1)$$

In this equation, we assume the chain transfer reaction of DEZ on ethylene polymerization is n times (corresponding reaction constant is $k_Z$), and the chain growth reaction is a first reaction of ethylene concentration ($k_p$). There are also other chain transfer reactions in the system ($k_{other}$). $\bar{M}_n^z$ in Equation 1 is the molecular weight of polyethylene in the presence of DEZ. $\bar{M}_n^o$ is the molecular weight when there is no DEZ in the polymerization system. k in Equation 1 is defined as $k=\frac{k_z\bar{M}_n^o}{k_p[E]}=\frac{k_z}{k_{other}}$.

According to Equation 1, all regression parameters, $k$ and $n$, are calculated and listed in Table 3. For all catalysts, the regression parameters $k$ and $n$ of copolymerization of ethylene or propylene with 1-hexene were smaller than those of ethylene or propylene homopolymerization, meaning that the introduction of the comonomer into the polymerization system reduces the efficiency of chain transfer by DEZ. In the study of heterogeneous catalysis, the increase of mass

**Table 3**. Regression parameters of the Equation 1 for ethylene or propylene polymerization.

| Cat | Polym. | ln *k* | *n* | Pearson's r |
|---|---|---|---|---|
| **1**[(a)] | homo- | 3.52 | 1.23 | 0.9993 |
| **1** | co- | 3.42 | 0.94 | 0.9883 |
| **2**[(a)] | homo- | 3.07 | 1.33 | 0.9918 |
| **2** | co- | 2.86 | 1.13 | 0.9048 |
| **3**[(a)] | homo- | 4.84 | 1.49 | 0.9962 |
| **3** | co- | 4.56 | 1.20 | 0.9999 |
| **4** | homo- | 3.98 | 0.82 | 0.9947 |
| **4** | co- | 3.82 | 0.49 | 0.9919 |

[(a)] Extracted from reference [28].

transfer resistance is considered to reduce the order of the apparent kinetics [29-30]. This may be the reason why the chain transfer order of copolymerization is lower than that of homopolymerization and propylene polymerization is lower than that of ethylene.

## CONCLUSION

Using diethyl zinc as the chain transfer agent, ethylene or propylene (co)polymerization were conducted by using metallocene catalysts. The molecular weight of polymer could be efficiently reduced. The chain transfer effect of DEZ was partly shielded by the substituent on the comonomer in ethylene polymerization. The shielding effect is more serious in propylene (co)polymerization, even homopolymerization, due to the alkyl substituent including the methyl on propylene monomer. Therefore, all regression parameters, concerning ethylene copolymerization and propylene homo- and copolymerization are smaller than those of ethylene homopolymerization. The present study not only studies the chain transfer effect of DEZ in ethylene or propylene polymerization, but also can guide the actual production of polyolefin wax. Through the regression equation, the product can be customized through polymerization conditions in the production of polyolefin wax.

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