

Tandem Catalysis of One Metallocene Catalyst Combined with Two Different Cocatalysts for Preparing Branched Polyethylene^{*}

Min Yang^{**}, Qin Li, Xiang-liu Li, Bo-wen Hu, Xiao-fang Dong, Jia-yan Qu, Bin-yuan Liu^{**},
Xi Wang and Xiao-yu Hao

Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, China

Abstract Tandem catalytic systems, consisting of ethylene bis(indenyl) zirconium dichloride with two different cocatalysts, alkylaluminum (diethylaluminum chloride or trialkylaluminum) and methylaluminoxane, were employed in preparing branched polyethylene from ethylene as sole monomer. The catalytic system *rac*-Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO exhibited high incorporation (29.0/1000C). The oligomerization and copolymerization reaction conditions in the tandem catalytic system, as well as the different cocatalysts, have effects on the catalytic activity and the properties of the obtained polymer, such as melting temperature, crystallinity, molecular weight and molecular weight distribution. Moreover, the oligomerization reaction condition is the main factor in altering the properties and structures of polyethylene.

Keywords: Tandem catalysis; Branched polyethylene; Metallocene; Alkylaluminum; Methylaluminoxane.

INTRODUCTION

Branched polyethylene such as linear low density polyethylene is more attractive because of its broad range of commodity applications and scientific values in preparing polyolefin with well-defined structure. It is commonly produced on industrial scales by the copolymerization of ethylene with α -olefin comonomer which comes from ethylene oligomerization. Since the same monomer ethylene was used in the steps of oligomerization and copolymerization, many strategies of the “tandem catalysis” technique have been developed to combine these two steps in one^[1, 2]. This one-pot process allows for oligomerization and copolymerization to be carried out in a single vessel without isolation of intermediates, thus avoiding stop-and-go syntheses and therefore affording an economical and environmental way of preparing branched polyethylene.

The early research of tandem catalysis involves two different traditional Ziegler-Natta catalysts and alkylaluminum cocatalyst^[1–5]. In further studies, the metallocene, especially the *ansa*-zirconocenes activated with methylaluminoxane (MAO) (or tris(pentafluorophenyl)borane) was used as the copolymerization component in the combination of Ziegler-Natta catalyst/trialkylaluminum^[6, 7]. Moreover, numerous investigations were paid on tandem catalytic systems comprising two or more metallocenes, metallocene catalyst/non-metallocene catalyst^[8–21]. The tandem catalytic systems consisting of two non-metallocenes were also reported^[22–24].

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^{**} Corresponding authors: Min Yang (杨敏), E-mail: polym@163.com

Bin-yuan Liu (刘宾元), E-mail: byliu@hebut.edu.cn

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For the tandem catalysis of ethylene, the presence of oligomerization active species and copolymerization active species is the key feature in one reaction system. Oligomerization active species oligomerize the ethylene to α -olefins, and copolymerization active species are responsible for polymerizing the ethylene and incorporating the α -olefins into the growing polymer chain. Well then, one catalyst precursor with two different cocatalysts also can form oligomerization active species and copolymerization active species to produce branched polyethylene. With this knowledge in mind, our group has reported a novel tandem catalyst, *i.e.* one catalyst precursor with two different cocatalysts^[25, 26]. These zirconium complexes exhibit a dual oligomerization/polymerization nature. They can be used as oligomerization catalyst with alkylaluminum to produce α -olefins, and also have been employed in producing polyethylene in the presence of methylaluminoxane or alkylaluminum. For the new tandem catalytic systems, the deep investigation is necessary.

Here, we selected one metallocene rac -Et(Ind)₂ZrCl₂ as the single catalyst precursor, alkylaluminum (AlEt₂Cl, Al(*i*-Bu)₃ or AlEt₃) as the oligomerization cocatalyst and MAO as the copolymerization cocatalyst, which composed the tandem catalytic systems of ethylene for preparing branched polyethylene. The effects of variables such as temperature, pressure, and type of alkylaluminum on the catalytic behavior for the tandem catalysis of ethylene and the resulting polyethylene microstructure and properties were investigated in detail.

EXPERIMENTAL

Materials

All manipulations of the air- and/or moisture-sensitive materials were carried out under a dry argon atmosphere in a glove box or using standard Schlenk techniques. Ethylene (polymerization grade) was provided by Daqing Petrochemical Complex (PetroChina). Catalyst rac -Et(Ind)₂ZrCl₂ was purchased from Aldrich and used as received. Cocatalysts AlEt₂Cl, AlEt₃, Al(*i*-Bu)₃ (Aldrich, 1.0 mol/L) and MAO (Albemarle, 1.4 mol/L) were used as received. Xylene (> 99.0%, TJ Chemical Reagents Company) was dried through an activated molecular sieve (4Å) then refluxed and distilled over sodium diphenylketyl complex prior to use. All other chemicals were obtained commercially and used as received.

Polymerization

The polymerization was carried out in a 500 mL stainless steel autoclave with mechanical stirring and a temperature and pressure controller. The autoclave was dried under vacuum at 150 °C for 60 min and cooled to room temperature under an argon atmosphere, then purged with dry argon two times and ethylene once. Then the xylene, a prescribed amount of catalyst solution and oligomerization cocatalyst solution were injected and then the mixture was maintained at the desired temperature (T_{oligo}) and ethylene pressure (P_{oligo}) of oligomerization. After 60 min, the pressure of autoclave fell to atmosphere pressure soon, the copolymerization cocatalyst solution was introduced into the reactor, and then ethylene ($P_{\text{co}} = 0.1$ MPa) was supplied to the reactor. The polymerization mixture was quenched by the addition of 10 vol% HCl/ethanol solution after 60 min. The obtained polymers were washed with water and ethanol, and then dried at 60 °C in vacuum for 8 h.

The oligomerization samples used for gas chromatography/mass spectrometry (GC-MS) were prepared with the following procedure: acetone was injected into the reactor to terminate the reaction, and then the resulting product was stocked in the close reactor for more than 2 h at -10 °C before being subjected to GC-MS analysis.

Characterization

The distribution of the oligomers was determined by GC-MS analysis using a TRACE-DSQ apparatus (Thermo Co.) with a CP-SIL5 capillary column and an HP-5971 mass spectrometer. The column temperature started at 50 °C (10 min) was raised at 10 K/min to 250 °C, and was kept at 250 °C for 30 min. The melting temperatures (T_m) and the fusion enthalpy (ΔH_f) of the polymers were determined by differential scanning calorimetry (DSC) with a DSC-Diamond (Perkin-Elmer Co.) operating at a heating rate of 10 K/min from 50 °C to 150 °C under an atmosphere of N₂, and T_m was determined in the second scan. The crystallinity (χ_c) was calculated from the heat of fusion, $(\Delta H_f / \Delta H_f^0) \times 100\%$, where ΔH_f^0 is the heat of fusion of folded-chain polyethylene (PE, 289.0 J/g)^[27].

The ^{13}C -NMR analysis was performed on a Bruker DMX-400 operating at 120 °C and 400 MHz. The polymer solutions were prepared in *o*-dichlorobenzene in a sample tube with a diameter of 5 mm. Gel permeation chromatography (GPC) analysis was conducted on Polymer Lab PL-220 instrument at 140 °C and 1.0 mL/min using polystyrene as standard, 1,2,4-trichlorobenzene was used as the solvent.

RESULTS AND DISCUSSION

Effect of Oligomerization Condition on the Tandem Catalysis

The oligomerization catalyst species and reaction condition in tandem catalysis of ethylene remarkably affect the kind of α -olefins and its distributions, and subsequently influence the copolymerization. The oligomerization reactions catalyzed by *rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$, *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl and *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_3$ were investigated in our previous researches^[28]. In these catalytic systems, there were no α -olefins produced by these catalytic systems at atmosphere pressure, while the oligomerization reactions occurred at the relatively high pressure and temperature. The selectivity of α -olefins and activity are different, which depend on the different cocatalyst and reaction condition. In these *rac*-Et(Ind) $_2$ ZrCl $_2$ /alkylaluminum systems, the oligomers were composed of C $_4$ –C $_{16}$ linear α -olefins, nonlinear α -olefins and alkanes. The 1-butene and 1-hexene were main products. The selectivities of linear α -olefins are 41%–81% (*rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$) and 62%–94% (*rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl). While, because of the lower selectivity of α -olefins (less than 73%) produced by *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_3$ ^[28], we just investigated the effect of *rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$ and *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl oligomerization systems on tandem catalysis. The percentage of linear α -olefins in total oligomers produced by *rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$ and *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl are also listed in the Table 1 and Table 2. The selectivity of linear α -olefins can help us to investigate the effect of oligomerization on tandem catalysis results.

Table 1. The effects of oligomerization conditions in *rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$ /MAO system^a

Run	$n(\text{Al}(\text{i-Bu})_3)/n(\text{Zr})$	T_{oligo} (°C)	P_{oligo} (MPa)	C $_4$ /C $_6$ /C $_{\geq 8}$ ^b (%)	A (10 ⁵ gPE/molZr·h)	T_{m} (°C)	χ_{c} (%)	M_{w} (10 ³)	MWD
1 ^c	0	0	0	0	9.7	131.6	69.0	–	–
2	150	90	1.4	26/3/12	9.3	127.5	33.3	–	–
3	150	110	1.4	37/13/12	8.4	120.7	28.5	3.0	18.0
4	150	150	1.4	60/15/4	4.8	114.6	21.0	2.6	13.6
5	150	110	1.0	29/5/14	7.3	124.2	30.9	–	–
6	60	150	1.4	61/6/3	5.4	120.2	22.6	3.1	16.8
7	250	150	1.4	64/14/3	5.7	112.0	15.8	2.0	6.8
8	350	150	1.4	53/20/4	5.2	113.4	17.1	–	–

^a *rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$ /MAO catalytic system; $V(\text{solvent}) = 100$ mL, $n(\text{Zr}) = 10$ μmol , $P_{\text{co}} = 0.1$ MPa, $n(\text{MAO})/n(\text{Zr}) = 250$, $T_{\text{co}} = 30$ °C, $t = 120$ min;

^b *rac*-Et(Ind) $_2$ ZrCl $_2$ /Al(*i*-Bu) $_3$ catalytic system; $V(\text{solvent}) = 50$ mL, $n(\text{Zr}) = 10$ μmol ; C $_4$: 1-butene, C $_6$: 1-hexene, C $_{\geq 8}$: sum of 1-octene, 1-decene, 1-dodecene, 1-tetradecene and 1-cetene;

^c *rac*-Et(Ind) $_2$ ZrCl $_2$ /MAO catalytic system; $V(\text{solvent}) = 100$ mL, $n(\text{Zr}) = 10$ μmol , $n(\text{MAO})/n(\text{Zr}) = 500$, $P = 0.1$ MPa, $T = 30$ °C, $t = 60$ min

Table 2. The effect of $n(\text{AlEt}_2\text{Cl})/n(\text{MAO})$ in Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl/MAO system^a

Run	$n(\text{AlEt}_2\text{Cl})/n(\text{Zr})$	C $_4$ /C $_6$ /C $_{\geq 8}$ ^b (%)	A (10 ⁵ gPE/molZr·h)	T_{m} (°C)	χ_{c} (%)
9	70	40/38/16	7.3	111.8	19.3
10	100	42/34/15	8.7	109.0	16.0
11	200	54/17/4	8.9	115.3	25.0
12	300	61/13/4	8.0	116.1	22.7
13	500	50/7/5	9.2	120.0	20.3

^a *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl/MAO catalytic system, $V(\text{solvent}) = 60$ mL, $n(\text{Zr}) = 50$ μmol , $T_{\text{oligo}} = 110$ °C, $P_{\text{oligo}} = 1.2$ MPa, $n(\text{MAO})/n(\text{Zr}) = 400$, $P_{\text{co}} = 0.1$ MPa, $T_{\text{co}} = 20$ °C, $t = 120$ min;

^b *rac*-Et(Ind) $_2$ ZrCl $_2$ /AlEt $_2$ Cl catalytic system; $V(\text{solvent}) = 40$ mL, $n(\text{Zr}) = 50$ μmol , $T_{\text{oligo}} = 110$ °C, $P_{\text{oligo}} = 1.2$ MPa; C $_4$: 1-butene, C $_6$: 1-hexene, C $_{\geq 8}$: sum of 1-octene, 1-decene, 1-dodecene, 1-tetradecene and 1-cetene

It's well known that the metallocene catalytic system $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{MAO}$ possesses pretty good copolymerization capacity and has been used as the copolymerization catalyst of tandem catalysis in previous works^[9, 17]. So MAO is a suitable copolymerization activator for tandem catalytic system. And then, the tandem catalytic systems $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{MAO}$, $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{AlEt}_2\text{Cl}/\text{MAO}$ and $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{AlEt}_3/\text{MAO}$ were used in preparing branched polyethylene from ethylene. At the fixed copolymerization condition, the tandem catalytic reactions of ethylene were carried out under different oligomerization reaction conditions, such as various oligomerization cocatalyst, molar ratio of Al/Zr, ethylene pressure and reaction temperature. The results are summarized in Table 1 and Table 2.

The polyethylenes prepared by $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{MAO}$ (Run 1) had typical thermal properties of HDPE, such as high melting temperature ($T_m = 131.6\text{ }^\circ\text{C}$) and high crystallinity ($\chi_c = 69.0\%$), which is accord with the previously papers^[9, 15, 17]. The addition of another alkylaluminum cocatalyst led to a significant decrease in the melting temperature and crystallinity of polymers. Seeing from Table 1 and Table 2, it is found that the oligomerization reaction conditions in tandem catalytic reactions have obvious influence on the melting temperature (T_m), crystallinity (χ_c) and molecular weight (M_w) of copolymer.

With the oligomerization stage reaction temperature increased from $90\text{ }^\circ\text{C}$ (Run 2) to $150\text{ }^\circ\text{C}$ (Run 4), as shown in Fig. 1, the T_m (χ_c) value of polymer produced by $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{MAO}$ decreased from $127.5\text{ }^\circ\text{C}$ (33.3%) to $114.6\text{ }^\circ\text{C}$ (21.0%). The T_m and χ_c of copolymer (Run 7) can be reduced to $112\text{ }^\circ\text{C}$ and 15.8%, when the oligomerization reaction was under higher ethylene pressure (1.4 MPa) and oligomerization temperature ($150\text{ }^\circ\text{C}$). These changes are consistent with the increase of linear α -olefins percentage. We observed the percentage of linear α -olefins increasing under a certain extent higher ethylene pressure and reaction temperature. As a result, more α -olefins were incorporated in the growing chains, which made crystallinity of polymers reduced. In $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{AlEt}_2\text{Cl}/\text{MAO}$ system, higher oligomerization Al/Zr molar ratio (Run 11–Run 13) caused the crystallinity of copolymer to increase. It is due to the percentage of α -olefins decreasing in oligomerization reaction stage.

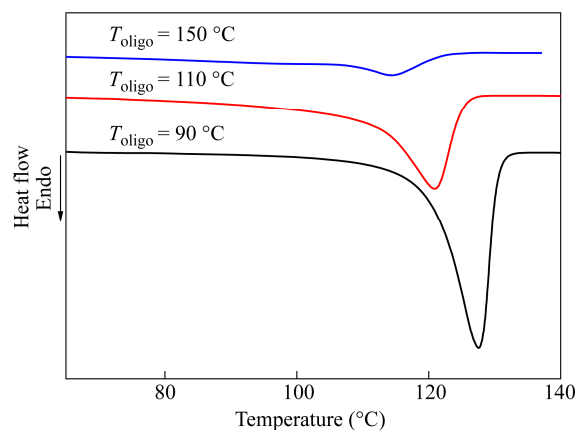


Fig. 1 DSC curves of polyethylenes obtained with $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{MAO}$ at different oligomerization temperatures (Run 2–Run 4)

From the Table 1 and Table 2, we can also see that the tandem catalytic activities obviously were lower than activity of $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{MAO}$ system. Based on previous results, it is found that α -olefin as comonomer may result in a negative “comonomer effect”. More α -olefins compete against ethylene in π -complexation with the active sites. When the rate of migratory insertion of α -olefin is slower than that of ethylene into the bond between metal and propagation chain, the ethylene polymerization rate may be decreased by the presence of α -olefins, then the activity of tandem catalysis decreases^[29].

The influences of the oligomerization $\text{Al}(i\text{-Bu})_3/\text{Zr}$ molar ratio on M_w and molecular weight distribution (MWD) were investigated, and the results are illustrated in Fig. 2. In $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{MAO}$ tandem catalytic system, with the increasing of $\text{Al}(i\text{-Bu})_3/\text{Zr}$ molar ratio from 60 to 250, molecular weight decreased from 3.1×10^5 (run 6) to 2.0×10^5 (run 7). Seeing from the results of oligomerization of $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3$ system, when the $\text{Al}(i\text{-Bu})_3/\text{Zr}$ molar ratio was changed from 60 to 250, the TOF (turn over frequency) of catalytic system increased from 3.4×10^5 g/molZr·h to 5.7×10^5 g/molZr·h, accompanied by the increase of α -olefins percentage^[28]. Therefore, more α -olefins participate in the copolymerization with ethylene and accelerate the transfer to comonomer reaction^[16], consequently leading to lower molecular weight copolymers. The decrease trend of molecular weight is typical for ethylene/ α -olefin copolymerization^[30].

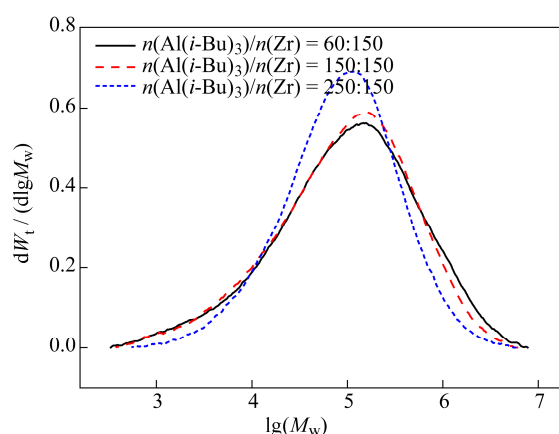


Fig. 2 The GPC curves of polyethylenes obtained with $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{MAO}$ in different $n(\text{Al}(i\text{-Bu})_3)/n(\text{Zr})$ (Run 4, Run 6 and Run 7)

Compared with these catalytic systems, it can be found that $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2/\text{AlEt}_2\text{Cl}/\text{MAO}$ system is better for producing branched polyethylene than other two systems, by reason of higher selectivity of α -olefins in the $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2/\text{AlEt}_2\text{Cl}$ system observed in our previous paper^[28]. At the same time, the results indicated that oligomerization reaction conditions have significant effects on the structure and properties of the copolymers.

Effect of Copolymerization Condition on the Tandem Catalysis

The tandem catalytic reactions of ethylene were carried out under different copolymerization reaction conditions, such as $n(\text{MAO})/n(\text{Zr})$ and copolymerization reaction temperature at the fixed oligomerization condition. The results are summarized in Table 3 and Table 4.

The effects of MAO/Zr molar ratio on the activity and properties of the copolymers were investigated in Table 3 (Run 14–19) and Table 4 (Run 20–22). The activity increased and then decreased with the $n(\text{MAO})/n(\text{Zr})$ increasing in the three tandem catalytic systems. However, the $n(\text{MAO})/n(\text{Zr})$ has slight effect on the thermal behavior of the resulting polymers. The slight effect results from the same selectivity of α -olefins, which produced at the same oligomerization condition. The molecular weight of polymer also depends on the $n(\text{MAO})/n(\text{Zr})$ ratio, and has the same changing trend of activity, as shown in Fig. 3. An appropriate quantity of copolymerization cocatalyst is in favor of the chain growing, and then causes higher molecular weights and activity. Under higher concentration of aluminium compound condition, a growing in amount of low molecular weight fraction, accompanied by the reducing of the high molecular weight fraction, is observed with the increase of $n(\text{MAO})/n(\text{Zr})$ from 400 to 800 in Fig. 3. The decreasing molecular weights of polymers and activity with increasing concentration of aluminium compound could be attributed to the chain-transfer reactions to the aluminium.

Table 3. The effects of copolymerization conditions on activity and properties of the copolymers

Run	Catalytic system	$n(\text{MAO})/n(\text{Zr})$	A (10^5 gPE /molZr·h)	T_m ($^{\circ}\text{C}$)	χ_c (%)
14	<i>rac</i> -Et(Ind) ₂ ZrCl ₂ /Al(<i>i</i> -Bu) ₃ /MAO ^a	250	5.7	112.0	15.8
15		500	6.4	113.4	16.8
16		1000	6.0	112.3	15.6
17		250	6.6	122.3	46.9
18	<i>rac</i> -Et(Ind) ₂ ZrCl ₂ /AlEt ₃ /MAO ^b	500	10.6	125.1	47.8
19		1000	6.7	123.5	46.0

$V(\text{solvent}) = 100$ mL, $n(\text{Zr}) = 10$ μmol , $P_{\text{co}} = 0.1$ MPa, $T_{\text{co}} = 30$ $^{\circ}\text{C}$, $t = 120$ min;

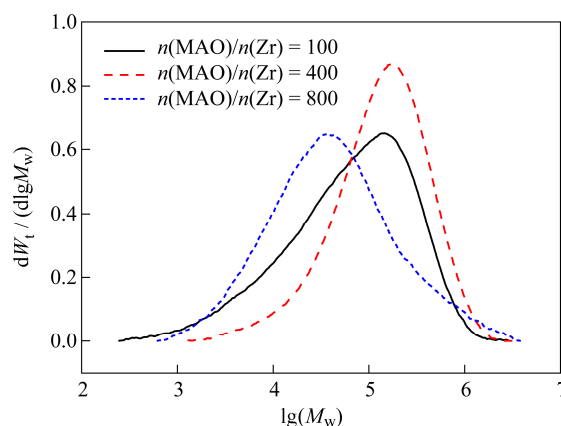
^a $n(\text{Al}(\text{i-Bu})_3)/n(\text{Zr}) = 250$, $T_{\text{oligo}} = 150$ $^{\circ}\text{C}$, $P_{\text{oligo}} = 1.4$ MPa;

^b $n(\text{AlEt}_3)/n(\text{Zr}) = 70$, $T_{\text{oligo}} = 100$ $^{\circ}\text{C}$, $P_{\text{oligo}} = 1.4$ MPa

Table 4. The effects of copolymerization conditions on activity and properties of the copolymers^a

Run	$n(\text{AlEt}_2\text{Cl})/n(\text{Zr})$	$n(\text{MAO})/n(\text{Zr})$	T_{co} ($^{\circ}\text{C}$)	A (10^5 gPE /molZr·h)	T_m ($^{\circ}\text{C}$)	χ_c (%)	M_w (10^5)	MWD
20	200	100	20	7.6	114.0	19.3	1.4	9.5
21	200	400	20	8.9	115.3	25.0	2.2	4.8
22	200	800	20	7.0	117.3	19.2	1.2	8.3
23	100	500	5	7.4	113.3	24.4	—	—
24	100	500	30	7.5	107.6	16.9	1.3	10.0
25	100	500	60	8.1	98.6	12.7	0.57	9.6
26	100	500	90	7.8	103.7	14.8	—	—
27	100	500	115	7.5	105.4	20.9	—	—

^a *rac*-Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO catalytic system; $V(\text{solvent}) = 60$ mL, $n(\text{Zr}) = 50$ μmol , $T_{\text{oligo}} = 110$ $^{\circ}\text{C}$, $P_{\text{oligo}} = 1.2$ MPa, $P_{\text{co}} = 0.1$ MPa, $t = 120$ min

**Fig. 3** The GPC curves of polyethylenes produced by *rac*-Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO with different $n(\text{MAO})/n(\text{Zr})$ ratios (Run 20 – Run 22)

The broad MWD are observed in these tandem catalytic systems, which is similar to the previously reports of tandem catalytic system^[11, 31, 32]. Taking into account the wide distribution of oligomers produced in the oligomerization reaction system, different α -olefins have different insertion reactivities and different transfer reactions to comonomer depending on their size, these nonuniform reaction conditions may contribute to the broad MWDs in these experiments^[31, 32]. While the polymer with a relatively broad or bimodal MWD is of benefit to the industrial processes^[33, 34].

In *rac*-Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO catalytic system (Table 4), suitable copolymerization temperature (60 $^{\circ}\text{C}$) made the T_m and χ_c of polymers decrease to 98.6 $^{\circ}\text{C}$ and 12.7%. This suggests that suitable copolymerization temperature promotes the copolymerization reaction of ethylene and α -olefins to produce branched polyethylene. However, too higher copolymerization temperature (115 $^{\circ}\text{C}$) caused T_m and χ_c of

polymers to increase, which may be due to the solubility reducing of ethylene and α -olefins in solution at high temperatures. On the other hand, high copolymerization temperature accelerated chain-transfer reactions, which made the molecular weight of polymers decrease. Due to the higher selectivity of α -olefins in rac -Et(Ind)₂ZrCl₂/AlEt₂Cl oligomerization system, the melting temperature and crystallinity of polymers produced by rac -Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO are lower than those of the other tandem catalytic systems, which is consistent with the aforementioned results in the “Effect of oligomerization condition on the tandem catalysis”.

NMR Characterization

The microstructures of the polymers were analyzed by ¹³C-NMR spectroscopy, and the number of branches of resulting polymer was calculated by the Galland's method^[35]. Figure 4 shows the ¹³C-NMR spectra of the polymers obtained with rac -Et(Ind)₂ZrCl₂/Al(*i*-Bu)₃/MAO (Run 7) and rac -Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO (Run 25).

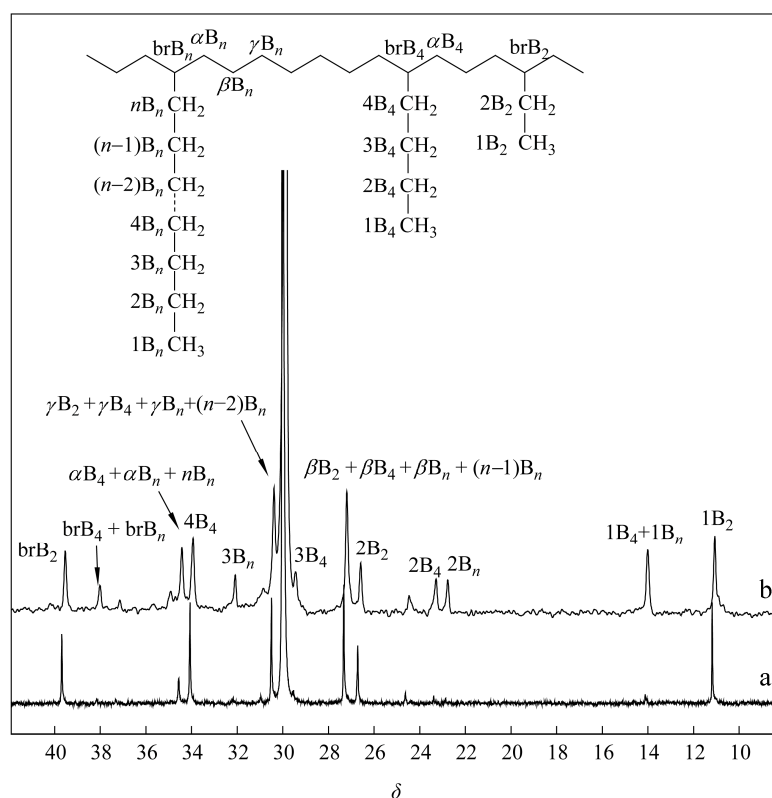
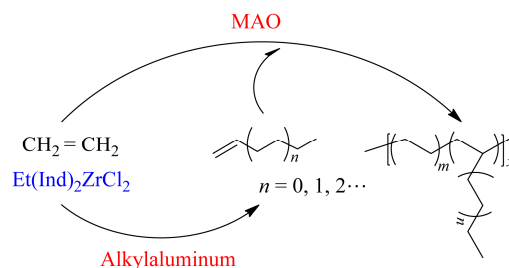


Fig. 4 ¹³C-NMR spectra of polyethylenes produced by (a) rac -Et(Ind)₂ZrCl₂/Al(*i*-Bu)₃/MAO (Run 7) and (b) rac -Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO (Run 25)

The ¹³C-NMR spectra of polymers (Run 7 and Run 25) show that the resulting polymers are branched polyethylenes. The polyethylene produced by rac -Et(Ind)₂ZrCl₂/AlEt₂Cl/MAO (Run 25) with total branches 29.0/1000C, including 52.0% ethyl (15.1/1000C), 33.4% butyl (9.7/1000C) and longer branches (4.2/1000C) of the total branches. On the whole, the distribution of the branches is in accord with the molar distribution of the α -olefins (butenes 46% and hexenes 37% of the total α -olefins) produced by rac -Et(Ind)₂ZrCl₂/AlEt₂Cl in ethylene oligomerization. The increasing of ethyl branches proportion in the polymer indicates that the incorporation of short chain 1-butane is much easier than that of longer α -olefin. Similarly, the total branches of the polyethylene produced by rac -Et(Ind)₂ZrCl₂/Al(*i*-Bu)₃/MAO is 15.9/1000C (Run 7), and mainly includes

81% ethyl branches (12.9/1000C), a few butyl branches (15%, 2.4/1000C) and longer branches (0.6/1000C). The relatively low branches of the polyethylene could be explained by the lower molar content of linear α -olefins produced in *rac*-Et(Ind)₂ZrCl₂/Al(*i*-Bu)₃ oligomerization system.

From the results and discussion, it can be found that the system *rac*-Et(Ind)₂ZrCl₂/alkylaluminum formed the oligomerization active species to oligomerize the ethylene to α -olefins, and the system *rac*-Et(Ind)₂ZrCl₂/MAO was responsible for polymerizing the ethylene and incorporating the α -olefins into the growing polymer chain to prepare branched polyethylene. This reaction process was shown in Scheme 1.



Scheme 1 Tandem catalyst system *rac*-Et(Ind)₂ZrCl₂/alkylaluminum/MAO for production of branched polyethylene using only ethylene as a monomer

CONCLUSIONS

In summary, it is feasible to prepare branched polyethylene from ethylene by combining one *rac*-Et(Ind)₂ZrCl₂ catalyst with two different cocatalysts, alkylaluminum (AlEt₂Cl, Al(*i*-Bu)₃ or AlEt₃) and MAO, as the tandem catalytic system. The different cocatalysts, as well as oligomerization conditions and copolymerization conditions in the tandem catalytic system, have effects on the polymerization activity, thermal property and structure of branched polyethylene. Compared with the copolymerization condition, the oligomerization reaction condition is the main factor in altering the properties and structures of polyethylene. The melting point, crystallinity, branching degree and molecular weight of the polyethylene can also be modified by the reaction conditions and various combinations of catalyst and cocatalysts. Furthermore, in our tandem catalytic system, the only catalyst precursor could avoid the synthesis cost of the other catalyst in previous tandem catalytic systems, at the same time, a part of MAO is replaced by inexpensive alkylaluminum. The tandem catalytic system may be a more economical and potentially useful way of preparing branched polyethylene.

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