Tandem Catalytic Systems: One Catalyst Combined with Two Different Activators for Preparing Branched Polyethylene with Ethylene as Single Monomer

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Introduction. Branched polyethylene such as linear low density polyethylene is more attractive because of its broad range of commodity applications and scientific value 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 1980s, many researches have been developed a new technique "tandem catalysis", which is a one-step method for preparing branched polyethylene from the single monomer of ethylene by the action of oligomerization and copolymerization catalyst precursors with one activator in the same reactor.[1] Since the linear α-olefins are formed *in situ*, the separation, transportation and storage of the comonomer are eliminated. So tandem catalysis could be a more economical way of preparing branched polyethylene. Up to now, various combinations of catalysts have been employed in tandem catalysis, such as two different Ziegler−Natta catalysts,[1,2] Ziegler−Natta catalyst/homogeneous catalyst,[3] or two or three different homogeneous catalysts.[4]

For the reported tandem catalytic systems, one catalyst oligomerizes the ethylene to α-olefins, and the second one is responsible for polymerizing the ethylene and incorporating the α-olefins into the growing polymer chain. Focusing on the essential of tandem catalysis of ethylene, we could suppose that the presence of two different active species is the key feature in one reaction system, i.e., oligomerization active species and copolymerization active species. Well then, can the combination of one catalyst precursor with two different activators form oligomerization active species and copolymerization active species to produce branched polyethylene? It appears to be very interesting to investigate the possibility of the new tandem catalytic system.

First, we need to select an appropriate catalyst which exhibits a dual oligomerization/polymerization nature. As we know, the metallocene bis(indenyl) zirconium dichloride (Ind_2ZrCl_2) and nonmetallocene *β*-diketonate zirconium complex have been employed in producing polyethylene in the presence of methylaluminoxane (MAO) as activator.[5] On the other hand, these zirconium complexes could also be used as oligomerization catalyst with alkylaluminum to produce α-olefins.[6] So, if we combine the zirconium complex with the two different activators (alkylaluminum and MAO), the catalytic system should meet the requirement to form two kinds of catalytic active species: oligomerization active species (zirconium complex/alkylaluminum) and copolymerization active species (zirconium complex/MAO) in one reactor. According to this idea, we attempted to design two novel tandem catalytic systems: one is composed of the commercial metallocene ethylene bis(indenyl) zirconium dichloride [$Et(Ind)_2ZrCl_2$] as single catalyst precursor, and diethylaluminium chloride ($AlEt_2Cl$) and MAO as the activators; the other is easily synthesized *β*-diketonate complex bis(dibenzoylmethanato) zirconium dichloride [$(dbm)_2ZrCl_2$] combined with $AlEt_2Cl$ and MAO (Figure 1). Herein, we will describe the two new tandem catalytic systems for preparing branched polyethylene in detail.

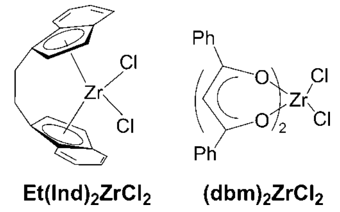

Figure 1. Structures of $Et(Ind)_2ZrCl_2$ and $(dbm)_2ZrCl_2$.

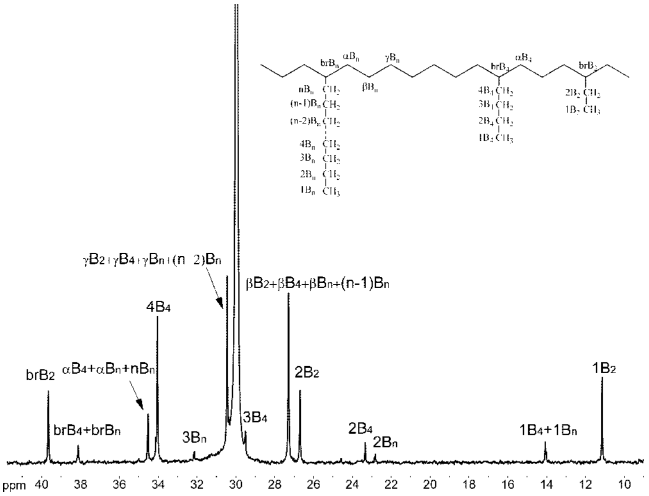

Figure 2. ^{13}C NMR spectrum of polyethylene produced by $Et(Ind)_2ZrCl_2/AlEt_2Cl/MAO$ (run 5).

Results and Discussion. Initially, the oligomerization reactions catalyzed by $Et(Ind)_2ZrCl_2/AlEt_2Cl$ and $(dbm)_2ZrCl_2/AlEt_2Cl$ were investigated. The oligomerization results are presented in Table 1. For catalytic system $(dbm)_2ZrCl_2/AlEt_2Cl$, the ethylene could be oligomerized to α-olefins (72.6%) at atmosphere pressure condition. However, there were no α-olefins produced by $Et(Ind)_2ZrCl_2/AlEt_2Cl$ at atmosphere pressure, while the oligomerization reaction could occur at the relatively high pressure and temperature, and the selectivity of α-olefins was 81.2%. From the distributions of oligomers obtained by the different zirconium complexes, it can be seen that the $Et(Ind)_2ZrCl_2/AlEt_2Cl$ system gave higher selectivity to C_4-C_{16} linear α-olefins (75.6%). The oligomers produced by $(dbm)_2ZrCl_2/AlEt_2Cl$ were composed by C_4-C_8 linear α-olefins (47.6%) and C_6-C_{12} nonlinear branched α-olefins (25.0%). On the basis of these preliminary results, the $AlEt_2Cl$ proved to be a fairly effective oligomerization activator for preparing α-olefins, and it could combine with zirconium complex to generate oligomerization active species in tandem catalysis of ethylene.

It is well-known that the metallocene catalytic system $Et(Ind)_2ZrCl_2/MAO$ possesses pretty good copolymerization capacity and has been used as the copolymerization catalyst of tandem catalysis in previous works.[4c,l,7] So MAO is a suitable

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Table 1. Results of Ethylene Oligomerization with Different Zirconium Complexes

run	catalyst	n(Al)/n(Zr)	T_p (°C)	P (MPa)	TOF[c]	1-butene (%)	1-hexene (%)	1-octene (%)	linear α-olefins (%)	α-olefins (%)
1[a]	Et(Ind)$_2$ZrCl$_2$	200	110	1.2	24.7	54.6	17.5	2.0	75.6	81.2
2[b]	(dbm)$_2$ZrCl$_2$	100	60	0.1	59.0	21.1	16.7	9.8	47.6	72.6

[a] Xylene (60 mL), catalyst = 50 μmol. [b] Toluene (50 mL), catalyst = 20 μmol. [c] TOF: turn over frequency, kg/molZr·h; polymerization time = 1 h.

Table 2. Results of Tandem Catalysis with Zirconium Complexes/AlEt$_2$Cl/MAO

run	catalyst	T_p (°C)	n(Al) /n(Zr)	AlEt$_2$Cl /MAO	activity (kg/molZr·h)	T_m[d] (°C)	χ_c[d] (%)	$\bar{M}_w$[e] (× 10^3)	MWD[e]
3	Et(Ind)$_2$ZrCl$_2$[a]	20	1000[c]	0	1269	130.7	68.3	20	2.5
4		20	1000	0.250	904	117.3	20.0	156	7.2
5		20	1000	0.333	879	113.3	22.3	110	7.1
6		20	1000	1	786	107.6	16.0	104	6.5
7	(dbm)$_2$ZrCl$_2$[b]	60	210	0	26.4	131.7	70.1	368	30.4
8		60	210	0.008	12.1	124.4	55.1	121	27.8
9		60	210	0.016	11.2	122.4	52.7	96	20.4
10		60	210	0.100	4.9	117.2	50.7	46	12.6

[a] Reaction conditions: xylene (60 mL), catalyst = 50 μmol, oligomerization temperature = 110 °C, oligomerization pressure = 1.2 MPa, copolymerization time = 1 h; [b] Reaction conditions: toluene (100 mL), catalyst = 120 μmol, oligomerization temperature = 60 °C, oligomerization pressure = 0.1 MPa, copolymerization time = 1 h. [c] MAO as the single activator in tandem catalytic reaction. [d] Measured by DSC. [e] Determined by GPC in 1,2,4-trichlorbenzene using PS standards.

copolymerization activator for tandem catalytic system. And then, two catalytic systems, Et(Ind)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO and (dbm)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO, were employed to test the possibility for preparing branched polyethylene from ethylene as single monomer. The results of tandem catalysis are summarized in Table 2.

The microstructures of the polymers were analyzed by ^{13}C NMR spectroscopy, and the number of branches of resulting polymer was calculated by the Galland's method.[8] Figure 2 shows the ^{13}C NMR spectrum of the polymer produced in run 5. The presence of ethyl branches could be confirmed by resonance at $\delta = 11.14$ ppm, 26.70 ppm and 39.66 ppm, and butyl branches by that at $\delta = 23.34$ ppm. The longer branches could be detected by the resonance at $\delta = 14.07$ ppm, 32.14 ppm and 39.66 ppm. The ^{13}C NMR spectrum shows that the resulting polymer is branched polyethylene with total branches 20.17/1000C, including 74% ethyl (14.90/1000C), 20% butyl (3.99/1000C) and 6% longer branches (1.28/1000C) of the total branches. On the whole, the distribution of the branches is in accord with the molar distribution of the α-olefins produced by Et(Ind)$_2$ZrCl$_2$/AlEt$_2$Cl in ethylene oligomerization (butenes 67% and hexenes 22% of the total α-olefins). 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, which is in agreement with the reported results of ethylene/α-olefin copolymerization catalyzed by Et(Ind)$_2$ZrCl$_2$/MAO.[9] Similarly, the total branches of the polyethylene produced by (dbm)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO is 4.30/1000C (run 10). The relatively low branches of the polyethylene could be explained by the lower molar content of linear α-olefins produced in oligomerization and the lower copolymerization capacity of β-diketonate zirconium in tandem catalysis.

We used MAO as the only activator with the zirconium complex to undergo the tandem catalytic reactions (run 3). The resulting polymer exhibits the typical thermal properties of high-density PE, such as high melting temperature T_m and high crystallinity χ_c. The addition of AlEt$_2$Cl led to a significant decrease in the melting temperature and crystallinity of polymer. In the examples of Et(Ind)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO, when the AlEt$_2$Cl/MAO molar ratio increased from 0 to 1, the polymer χ_c value effectively reduced from 68.3% ($T_m = 130.7$ °C, run 3) to 16.0% ($T_m = 107.6$ °C, run 6). The reductions of melting temperature and crystallinity are assigned to the higher amount of α-olefins produced and incorporated, and further testified that the resulting polymers are branched polyethylene. From the Table 2, we can also see that the tandem catalytic activities obviously decreased with the increase of AlEt$_2$Cl/MAO molar ratio. The trend is in accord with the negative "comonomer effect" of ethylene/α-olefin copolymerization. With the increase of AlEt$_2$Cl/MAO molar ratio, more α-olefins compete against ethylene in π-complexation with the active sites. If 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.[10]

Moreover, there is a clear effect of AlEt$_2$Cl/MAO molar ratio on the molecular weight ($\bar{M}_w$) and molecular weight distribution (MWD). When the AlEt$_2$Cl/MAO molar ratio was changed from 0 to 0.1 in (dbm)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO tandem catalytic system, $\bar{M}_w$ decreased from 368 × 10^3 to 46 × 10^3. A different phenomenon is observed in Et(Ind)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO catalytic system. The $\bar{M}_w$ increased first from 20 × 10^3 (homopolymer) to 156 × 10^3, a further increase of the AlEt$_2$Cl/MAO molar ratio caused the slightly decrease of molecular weight. Compared with all tandem reaction cases, the decrease trend of $\bar{M}_w$ and MWD is typical for ethylene/α-olefin copolymerization.[10,11] This may be in respect that a larger fraction of oligomerization activator will produce more α-olefins in the reaction system and accelerate a transfer to comonomer reaction,[4i,12] and then, the molecular weight of the polymer will decrease with the enhancement of AlEt$_2$Cl/MAO molar ratio. Therefore, it should be possible for this approach to generate many branched polyethylenes with tailored properties for specific applications by simply adjusting the ratio of the two activators.

The broad molecular weight distributions are observed in the two tandem catalytic systems, which is similar to the previously reports of tandem catalytic system.[4e,13] Taking into account the wide distribution of oligomers produced in the reaction system, different α-olefins display different insertion reactivities depending on their size, and different α-olefins bring on the different transfer reactions to comonomer, these nonuniform reaction conditions may contribute to the broad MWDs in these experiments.[13a] The other possible reason is that the cooperative action of oligomerization and copolymerization in tandem catalysis is not optimized to generate polymer with a homogeneous structure.[13a] The much broader MWDs of the polymers produced by (dbm)$_2$ZrCl$_2$/AlEt$_2$Cl/MAO correspond with that of the homopolymer by (dbm)$_2$ZrCl$_2$/MAO (run 7), which indicates that this β-diketonate catalyst behaves as a multiple-site type in the course of the polymerization reaction.[14]

Analogous cases of polymers with broad MWD can be seen from other reports in ethylene polymerization or styrene polymerization catalyzed by β-diketonate catalysts.[14] While the polymer with a relatively broad or bimodal MWD is of benefit to the industrial processes.[15]

In summary, it is feasible to prepare branched polyethylene from ethylene by combining $Et(Ind)_2ZrCl_2$ (or nonmetallocene $(dbm)_2ZrCl_2$) with two different activators ($AlEt_2Cl$ and MAO) as the tandem catalytic system. The results of polymerization clearly confirm that the presence of oligomerization active species and copolymerization active species in tandem catalytic system is the key feature for preparing branched polyethylene. So, tandem catalysis of ethylene is not limited to the combination of two or more catalysts, and the single catalyst precursor with two different activators can also be used as the tandem catalytic system to produce branched polyethylene *in situ*. Furthermore, in our tandem catalytic system, the catalyst precursor could be selected from commercial metallocene to easily synthesized nonmetallocene, which makes this method possess general application value for preparing branched polyethylene.

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Supporting Information Available: Text giving general experimental procedures and figures showing the GC spectra of oligomers, selected ^{13}C NMR spectra, and DSC and GPC curves for the resultant polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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