

Synthesis of branched polyethylene from ethylene stock by an interference-free tandem catalysis of $\text{TiCl}_4/\text{MgCl}_2$ and iron catalyst

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Abstract

An interference-free tandem catalysis based on iron catalyst and $\text{TiCl}_4/\text{MgCl}_2$, activated by MAO, was used to prepare branched polyethylene by polymerization of ethylene. No obvious deactivation due to the side reaction of catalysts and cocatalysts was detected during the reaction process, which commonly existed in tandem catalytic systems based on conventional Ziegler–Natta catalysts. A series of branched polyethylene with different properties have been prepared by adjusting of reaction temperature, Fe/Ti molar ratio and the amount of MAO used. The alteration of oligomers concentration in the reaction system, by changing of reaction conditions, led to the products with different branching degrees, thus the thermal properties and molecular weight. The products obtained in toluene at lower Fe/Ti ratios exhibited better morphology than those obtained at higher Fe/Ti ratios.

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Keywords: Branched; Polyethylene (PE); Copolymerization; Catalyst

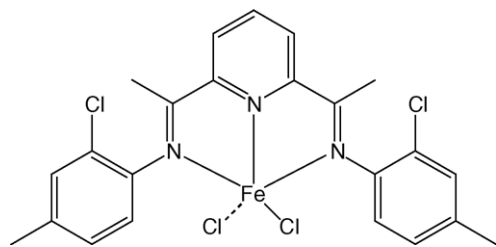
1. Introduction

Polyethylene with short-chain branches, known as linear low-density polyethylene (LLDPE), is an important member of the family of polyethylenes and has become of interest to plastic industry in the recent past. Compared with high density polyethylene (HDPE), LLDPE exhibits a lower melting point, lower crystallinity, and lower density due to the presence of short-chain branches with controlled length and frequency on the polymer backbone, which effectively enhance the mechanical strengths of polyethylene products, such as the stiffness, stress-crack resistance, tensile strength, and most importantly, processability.

Branched polyethylene is conventionally produced by ethylene copolymerization with α -olefin comonomer, such as 1-butene, 1-hexene, and 1-octene with Ziegler–Natta catalysts or single-site catalysts. In the 1980s, Beach and Kissin [1] and Kissin and Beech [2] reported a one-step method for producing branched polyethylene from only ethylene using a dual function catalytic system, which is well known as tandem reaction or in situ copolymerization. In this procedure, a tandem reaction is carried out by two catalysts: 1-alkene is produced by one catalyst from ethylene oligomerization and is copolymerized by the other in situ with ethylene to produce LLDPE. The most interesting advantage over common approaches is that only ethylene is used. The products with different properties could be obtained just by adjusting reaction conditions and the molar ratio of two catalysts.

There were three kinds of tandem catalytic systems reported: Ziegler–Natta catalysts [1,2], single-site catalysts

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Scheme 1.

[3–15] and well defined single-site catalysts [16–20]. Recently, many different tandem catalytic systems consisting of single-site ethylene polymerization and oligomerization catalysts were disclosed for the production of branched polyethylenes. But no Ziegler–Natta tandem catalytic systems besides Beach and Kissin’s work was reported to produce LLDPE in past years because of their poor compatibility due to the deactivation caused by the side reactions of catalysts and cocatalysts could be totally avoided because only MAO was used as cocatalyst. In addition, only ethyl-branched polyethylene was obtained in Beach and Kissin’s work. Here we report a new tandem catalysis, which comprises $\text{TiCl}_4/\text{MgCl}_2$ (**2**) as copolymerization catalyst and $[(2\text{-ArN}=\text{C}(\text{CH}_3))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ ($\text{Ar} = 2\text{-Cl-4-CH}_3\text{C}_6\text{H}_3$) (**1**) (Scheme 1) as oligomerization catalyst, to synthesize branched polyethylene with both short and long branches, which always exhibit good processability and mechanical properties. Methylaluminoxane (MAO) was used as the sole cocatalyst to eliminate the interference caused by multi-cocatalysts used. The polymerization results and properties of branched polyethylenes are discussed in detail.

2. Experimental

2.1. Materials

The oligomerization catalyst (**1**), $[(2\text{-ArN}=\text{C}(\text{CH}_3))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ ($\text{Ar} = 2\text{-Cl-4-CH}_3\text{C}_6\text{H}_3$) (Scheme 1), was synthesized and characterized as shown in reference [21]. Ziegler–Natta catalyst, $\text{TiCl}_4/\text{MgCl}_2$ (**2**) ($\text{Ti} = 4.77$ wt.%), was prepared in the following manner [22]: a reactor equipped with a stirrer was purged with nitrogen two to three times. Tributyl phosphate (0.1 mol) and dried magnesium chloride (0.05 mol) were added to the reactor under stirring and then the reaction temperature was increased to 80°C . After 2 h, semitransparent solution was obtained. Absolute ethyl alcohol (0.03 mol) was added into the reaction system when the temperature dropped to room temperature. After stirring for half an hour, phthalic anhydride (0.0075 mol) was introduced into the reactor and then the temperature was increased to 80°C and kept for 1 h. The solution obtained was dropped into TiCl_4 (0.9 mol) in another reactor at -5°C . The reaction temperature was increased to 80°C and the suspension obtained was stirred for 3 h. The hot liquid was removed and

the solid left was washed with 1,2-dichloroethane for three times and hexane for two times. Catalyst **2** was obtained as brown yellow powder by drying the solid under vacuum for more than 6 h at 50°C .

MAO solution (1.4 mol/L in toluene) was purchased from Albemarle Company. Polymerization grade ethylene and triethylaluminum (TEA) solution in heptane (1.8 mol/L) were obtained from Yanshan Petro-chemical Company, Sinopec, China. Toluene was distilled from sodium/benzophenone and degassed. All other chemicals were obtained commercially and used as received.

2.2. Polymerization/oligomerization of ethylene

A 250 mL dried three-necked flask with a stirring bar was purged with ethylene two or three times. Then 100 mL of toluene and a prescribed amount of MAO were injected and the mixture was magnetically stirred at different temperatures. The ethylene monomer was continuously fed in and its pressure was maintained at 0.1 MPa by an electromagnetic valve, and 2 min later, the polymerization was started by adding the suspensions of catalysts in toluene. The polymerization was terminated by the addition of 10 wt.% acidified ethanol and the resulting material was dried under vacuum for 6 h. The oligomerization of ethylene was similarly conducted.

2.3. Characterization

The distribution of oligomers was determined by GC-MS analysis using an HP-5890 apparatus with an HP-1 capillary column (30 m \times 0.25 mm) and an HP-5971 mass spectrometer. The column temperature started at 35°C (10 min), heated at a rate of $10^\circ\text{C}/\text{min}$ to 220°C and kept at 220°C for 10 min. ^{13}C nuclear magnetic resonance (^{13}C NMR) analysis was performed on a Bruker AM-300 spectrometer operating at 120°C and 75 MHz. The polymer solutions were prepared in *o*-dichlorobenzene in a sample tube 5 mm in diameter. The melting points (T_m) and the crystallinity (X_c) of polymers were determined by differential scanning calorimetry (DSC) using a DSC 7A (Perkin-Elmer) operating at a heating rate of $10^\circ\text{C min}^{-1}$ from 30°C to 160°C , and T_m was determined in the second scan. Gel permeation chromatography (GPC) was carried out on a Waters-300 instrument at 140°C and 1.0 mL/min. 1,2,4-Trichlorobenzene was used as solvent. Scanning electronic microscope (SEM) images were taken on a JEOL JSM-6700F microscope.

3. Results and discussion

3.1. Ethylene oligomerization with **1**/MAO

Activated by MAO, catalyst **1** exhibited high catalytic activities and most of the products (>94%) were α -olefins as shown in Table 1. As the temperature was increased from

Table 1
Ethylene oligomerization with 1/MAO

Run	Temperature (°C)	Al/Fe	Yield (g)	Activity (10^6 g/mol Fe h)	α	C ₄ (%)	C ₆ (%)	\geq C ₈ (%)	α -Olefin (%)
1	30	1400	12.10	24.2	0.55	17.4	22.6	60.0	>94
2	40	1400	10.05	21.0	0.55	–	–	–	>94
3	50	1400	7.80	13.6	0.54	23.9	23.8	52.3	>96
4	60	1400	4.50	9.00	0.53	29.4	24.6	46.0	>96
5	70	1400	1.45	2.90	0.51	30.4	24.6	45.0	>95
6	60	420	4.45	8.90	0.52	–	–	–	>95
7	60	700	4.25	8.50	0.53	–	–	–	>94
4	60	1400	4.50	9.00	0.53	29.4	24.6	46.0	>96
8	60	2100	4.05	8.10	0.52	–	–	–	>94
9	60	2800	4.00	8.00	0.53	29.1	24.2	46.7	>95

Reaction conditions: Fe: 1 μ mol; ethylene pressure: 0.1 MPa; reaction time: 30 min; 50 mL toluene as solvent; MAO as cocatalyst.

30 °C to 70 °C, the catalytic activities were decreased from 24.2×10^6 g/mol Fe h to 2.90×10^6 g/mol Fe h. The activities were not significantly changed when the Al/Fe molar ratio was increased from 420 to 2800. The 1-butene (C₄) and 1-hexene (C₆) contents in weight were increased from 40% to 55% of the total 1-olefins.

3.2. Ethylene polymerization with 2/MAO

Ziegler–Natta catalysts were conventionally activated by alkylaluminium. But catalyst **2** could be also activated by commercial MAO. The ethylene polymerization results under different reaction conditions are summarized in Table 2. The catalytic activities were increased to the maximum at 3 mL MAO and 50 °C. This means that Ziegler–Natta catalyst (catalyst **2**) could be combined with the iron oligomerization catalyst together as a tandem catalytic system, and the side reactions due to different cocatalysts could be totally avoided because only MAO was used as cocatalyst.

3.3. Ethylene absorption curves with tandem catalytic system 1/2/MAO

Activated by MAO, catalysts **1** and **2** were combined together as a tandem catalytic system for ethylene polymerization to prepare branched polyethylene as shown in Scheme 2.

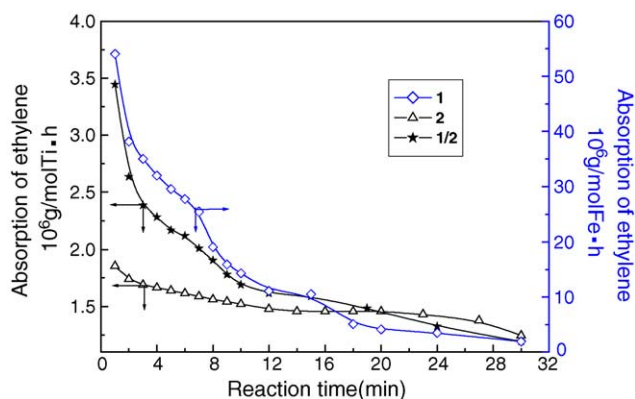
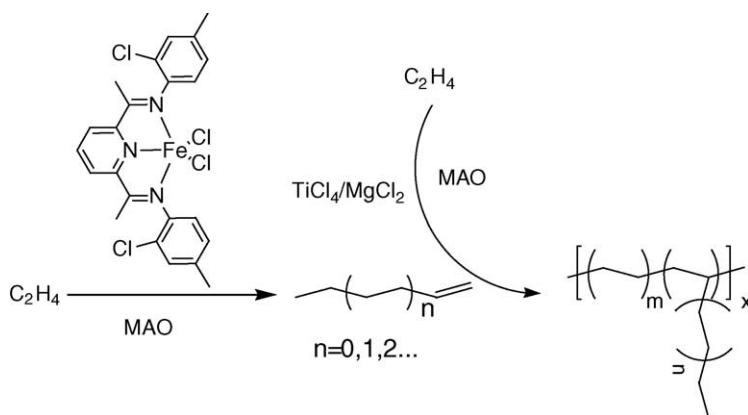


Fig. 1. The absorption curves of ethylene obtained from **1** (run 3 in Table 1), **2** (run 3 in Table 2) and **1/2** (run 2 in Table 3).

No interference between catalysts and cocatalyst was detected during the process of polymerization, which could be proved by the curves of ethylene absorption obtained from 1/MAO, 2/MAO and 1/2/MAO as shown in Fig. 1. The rate of ethylene absorption into the 2/MAO system hardly decreased during the whole reaction process. But the rate of ethylene absorption into the 1/MAO system decreased rapidly, and was close to zero at the end of the reaction. The tandem catalytic system 1/2/MAO exhibited the same trend in ethylene absorption as 1/MAO at the beginning, and retained an



Scheme 2.

Table 2
Ethylene polymerization results with catalyst **2**/MAO

Run	MAO	Temperature (°C)	Yield (g)	Activity (10 ⁶ g/mol Ti h)	<i>T_m</i> (°C)	<i>X_c</i> (%)
1	1	50	7.73	1.29		
2	2	50	8.67	1.44	132.0	63.5
3	3	50	8.75	1.46		
4	5	50	8.23	1.37		
5	2	40	6.43	1.07		
6	2	50	8.67	1.44	132.0	63.5
3	2	60	8.01	1.33		
7	2	70	7.76	1.29		

Reaction conditions: Ti: 12 μmol; reaction time: 30 min; ethylene pressure: 0.1 MPa; 100 mL toluene as solvent; MAO as cocatalyst.

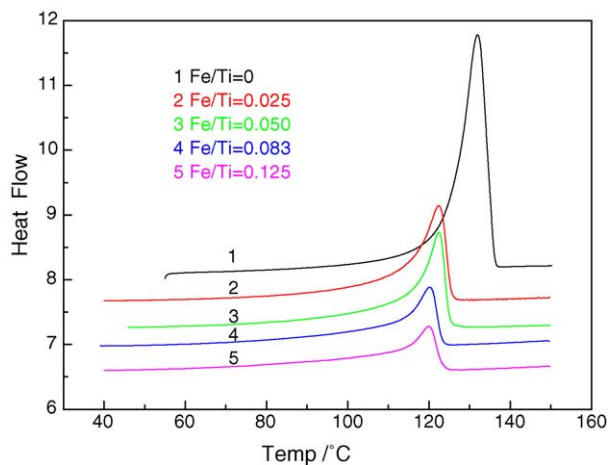


Fig. 2. The effect of Fe/Ti on the DSC curves of products.

ethylene absorption rate as high as **2**/MAO at the end of the reaction. This result indicated that **1** and **2** showed their own ethylene absorption behavior independently during the reaction process.

3.4. Ethylene polymerization with tandem catalytic system **1/2**/MAO

The ethylene polymerization with the tandem catalytic system (**1/2**), activated by MAO, was investigated and the

Table 3
Ethylene polymerization with **1/2**/MAO

Run	Ti (μmol)	Fe (μmol)	Fe/Ti	MAO (mL)	Temperature (°C)	Yield (g)	Activity (10 ⁶ g/mol Ti h)	<i>T_m</i> (°C)	<i>X_c</i> (%)	Mw (×10 ³) (Mw/Mn)	Branching (C/1000)			
											C ₂	C ₄	≥C ₆	Total
1	12	1	0.083	2	40	10.12	1.69	115.9	16.4	905(10.6)	34.9	17.1	7.0	59.0
2	12	1	0.083	2	50	9.13	1.52	120.2	24.1	830(13.3)	25.2	16.0	7.3	48.5
3	12	1	0.083	2	60	9.05	1.51	123.7	33.8					
4	12	1	0.083	2	70	3.92	0.65	124.0	34.3					
5	12	1	0.083	1	50	5.48	0.91	115.5	7.2					
2	12	1	0.083	2	50	9.13	1.52	120.2	24.1	830(13.3)	25.2	16.0	7.3	48.5
6	12	1	0.083	3	50	10.75	1.79	120.2	32.0		23.7	14.9	6.4	45.0
7	12	1	0.083	5	50	13.15	2.19	120.8	40.0	807(8.9)	24.2	13.6	4.2	42.0
8	12	0.3	0.025	2	50	12.14	2.02	122.4	34.5					
9	12	0.6	0.050	2	50	13.70	2.28	122.4	34.3	897(11.6)	5.2	3.6	1.7	10.5
2	12	1.0	0.083	2	50	9.13	1.52	120.2	24.1	830(13.3)	25.2	16.0	7.3	48.5
10	12	1.5	0.125	2	50	8.80	1.47	119.9	22.2					

Reaction conditions: reaction time: 30 min; ethylene pressure: 0.1 MPa; 100 mL toluene as solvent.

results are summarized in Table 3. The catalytic activities of **1/2**/MAO under most of reaction conditions were higher than those of **2**/MAO. The *T_m* and crystallinity (*X_c*) of polymers obtained from **1/2** were lower than those obtained from **2**/MAO. The catalytic activities of the tandem reaction slightly decreased with increasing temperature from 40 °C to 60 °C, and decreased sharply when the temperature was raised to 70 °C. It is well known that the introduction of α-olefins in a certain range results in an increase in the polymerization activity, which is called a comonomer effect. As temperature was increased from 40 °C to 60 °C, the activity of **1** decreased rapidly [21], but the activity of **2** hardly changed. So the tandem reaction activity decreased as reaction temperature increased, which led to the decrease in oligomers concentration in the reaction system. The activity at 70 °C was only half of that obtained with **2**/MAO under the same conditions. This could attribute to the deactivation of catalysts **1** and **2** at higher reaction temperature as well as the comonomer effect. The decrease in the comonomer concentration caused by the elevation of reaction temperature also resulted in the decrease in branching degrees and the improvement of thermal properties of the products as shown in Table 3.

It has been revealed that the properties of polyethylene could be altered just by adjusting the Fe/Ti molar ratio in tandem catalysis. The yield attained a maximum at Fe/Ti molar ratio=0.05 when the Fe/Ti molar ratios were changed from 0.025 to 0.125. But the thermal properties of prod-

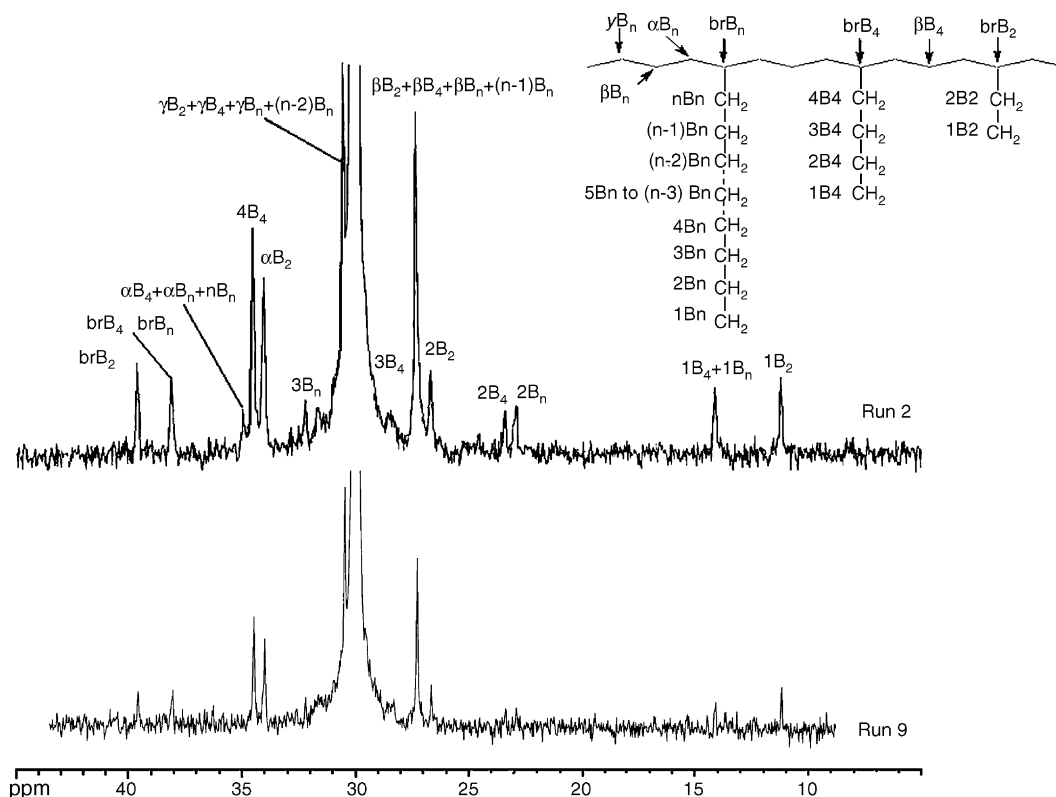


Fig. 3. ^{13}C NMR of polyethylene prepared by tandem catalysts (runs 2 and 9 in Table 3).

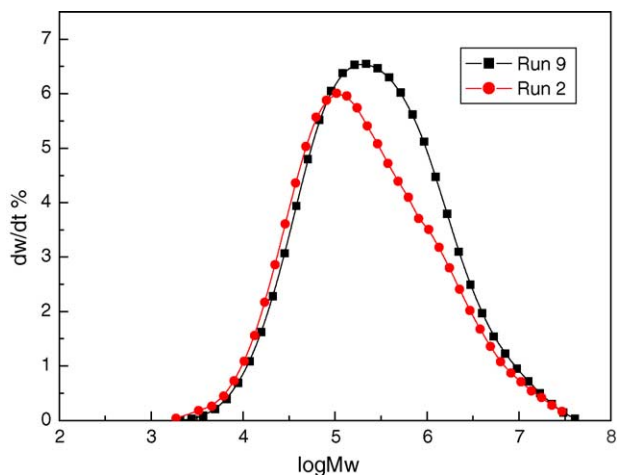


Fig. 4. GPC curves of polyethylene prepared by tandem catalysts (runs 2 and 9 in Table 3).

ucts deteriorated as shown in Fig. 2 and branching degrees increased. The introduction of comonomer could increase the catalytic activities in a certain range, but too much comonomer would inhibit the reaction of ethylene with Ti active species, which leads to the decrease in catalytic activities [23]. All the results indicated that increased oligomerization catalyst leads to an increase in branching degrees but there was an adaptable Fe/Ti molar ratio for the catalytic activity.

The effect of MAO on the catalytic activities and product properties was also studied. When the amount of MAO used was increased from 1 mL to 5 mL, the tandem reaction activities were improved from 0.91×10^6 g/mol Ti h to 2.16×10^6 g/mol Ti h. The melting point of product was increased from 115.5°C to 120.2°C when the amount of MAO was increased from 1 mL to 2 mL. Above that, the branching degrees decreased and thermal properties improved. The cocatalyst was not enough to activate all the active species of catalysts 1 and 2 when 1 mL MAO was introduced. So the product obtained possessed lower melting point and crystallinity, which also indicate that the shortage of cocatalyst affect catalyst 2 more deeply than catalyst 1. When there was enough cocatalyst, the introduction of more MAO exhibited negligible effect on the activity of 2, but led to some reduction of the activity of 1 as shown in Table 2. This could account for the change of products properties when the amount of MAO was increased from 2 mL to 5 mL.

The branching degrees and molecular weight of resulting polymers were measured from ^{13}C NMR and GPC, respectively. The ^{13}C NMR spectrum and GPC curve of branched polyethylene obtained (runs 2 and 9 in Table 3) are presented in Figs. 3 and 4. According to the literature [24], the presence of ethyl branches could be confirmed by resonance at $\delta = 11.19$ ppm, 26.67 ppm and 39.64 ppm and butyl branches by that at $\delta = 23.40$ ppm. The longer branches ($n \geq 2$) could be detected by the signal at $\delta = 14.12$ ppm, 32.21 ppm and 38.13 ppm. The ^{13}C NMR spectrum showed that the obtained

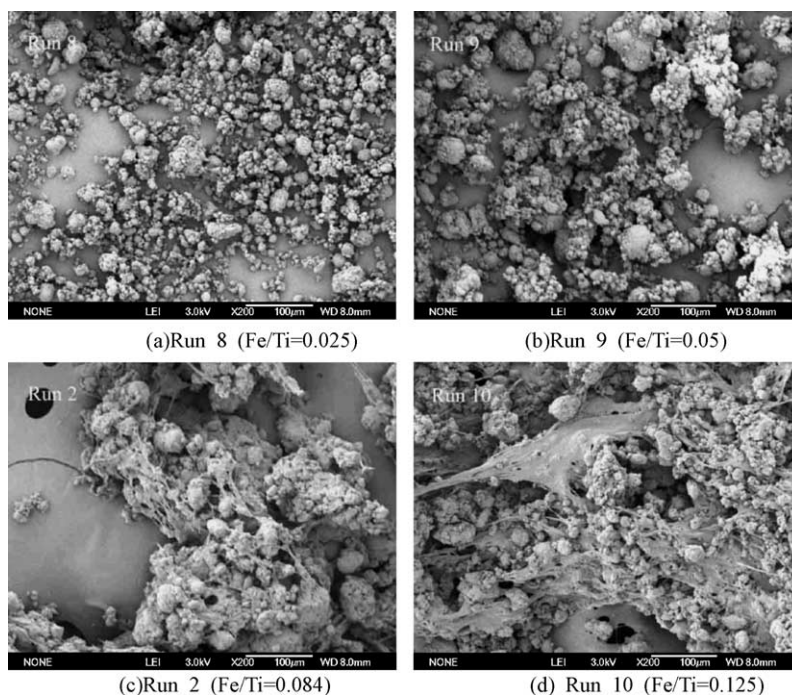


Fig. 5. The morphology of products obtained at different Fe/Ti molar ratios in toluene: (a) run 8 (Fe/Ti = 0.025); (b) run 9 (Fe/Ti = 0.05); (c) run 2 (Fe/Ti = 0.084); (d) run 10 (Fe/Ti = 0.125).

polymer was branched polyethylene with total branches from 10.5/1000C to 59.0/1000C, including ethyl (about 50%), butyl (about 30%) and longer branches (about 20%). The GPC of products (runs 2 and 9) exhibit a broad unimodal curve as shown in Fig. 4. The molecular weight of the products was in the range of 807,000–905,000 and the molecular weight distributions were in the range of 8.9–13.3, which would provide excellent mechanics performance and processability for the products. All the results indicated that the two catalysts could be combined together to prepare short and long chains branched polyethylene without any interference in the tandem reaction.

The morphology of products prepared at different Fe/Ti molar ratios was studied and SEM images are presented in Fig. 5. The products exhibited distinct morphology at lower Fe/Ti molar ratios, which replicated the global shape of MgCl_2 support. When the Fe/Ti molar ratio was increased, more products with morphology as produced in homogeneous systems were obtained as shown in Fig. 5(c and d). This could be attributed to the better solubility of polyethylene with more branches in toluene.

4. Conclusions

A tandem catalytic system 1/2/MAO was used to prepare branched polyethylene with short and long chain branches under different reaction conditions. Interference between catalysts and cocatalysts was avoided because MAO was used as the sole cocatalyst. The catalytic activities and product properties obtained under different reaction conditions were in-

vestigated and mainly affected by the alteration of oligomers concentration in the reaction system. The products obtained at lower Fe/Ti molar ratios showed more distinct morphology than those obtained at higher Fe/Ti ratios due to the high solubility of branched polyethylene in toluene.

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