

Synthesis of Branched Polyethylene by *In Situ* Polymerization of Ethylene with Combined Iron Catalyst and Ziegler–Natta Catalyst

Zhanxia Lu,^{1,2,3} Zhicheng Zhang,^{1,2} Yang Li,³ Chunhong Wu,³ Youliang Hu¹

¹Joint Laboratory of Polymer Science and Materials, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

²Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

³Research Institute of Beijing Yanshan Petrochemical Co., Ltd., Beijing 102500, People's Republic of China

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ABSTRACT: 2,6-Bis(imino)pyridyl iron catalyst and traditional Ziegler–Natta catalyst were combined together as tandem catalytic system, activated with the mixture of TEA and MAO, and used for synthesis of branched polyethylene by *in situ* polymerization of ethylene. The branched polyethylene with branches from 8/1000C to 29/1000C was produced by adjusting reaction conditions: the amount of TEA, MAO, iron catalyst used, and reaction temperatures. Not only the short branches such as ethyl and butyl but also the longer

branches (hexyl and longer than hexyl) were detected in the products. The products exhibited higher molecular weight and broader molecular weight distribution than those obtained from metallocene catalysts, which would provide the materials excellent mechanical properties and processability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2898–2903, 2006

Key words: iron catalyst; Ziegler–Natta; *in situ* polymerization; branched polyethylene

INTRODUCTION

Linear low-density polyethylene (LLDPE), known as branched polyethylene, is mainly produced by ethylene copolymerization with α -olefin comonomer, such as 1-butene, 1-hexene, and 1-octene with Ziegler–Natta catalyst or single-site catalysts. The high cost of α -olefin comonomer limits its application in industry greatly. In the 1980s, the technique of using dual-functional catalyst system, known as tandem catalytic systems, was reported by Beach¹ and Kissin² as a one-step method to produce LLDPE from sole ethylene stock. In this procedure, a tandem reaction was carried out between two catalysts: 1-alkene was produced by one catalyst from ethylene oligomerization and copolymerized by the other one *in situ* with ethylene to produce LLDPE. The only ethylene monomer used was the most interesting advantage over common approach. In addition, the properties of products could be altered just by adjusting reaction conditions and the molar ratio of two catalysts.

There are about three kinds of tandem catalytic systems reviewed by Bazan et al.,³ such as Ziegler–

Natta catalysts,^{1,2} single-site catalysts,^{4–13} and well-defined single-site catalysts.^{14,15} Recently, many different single-site tandem-action catalytic systems^{16–21} were introduced for the production of branched polyethylene. Owing to the high cost of this new approach in the synthesis of LLDPE by single-site catalysts, the development of this technique in Ziegler–Natta catalysts would allow us to implement the tandem technique in existing industrial processes. No further work was reported to prepare LLDPE with Ziegler–Natta catalysts as the tandem catalysis, due to their poor compatibility with other catalysts and cocatalysts. In their work, some ethylene dimerization catalysts and supported TiCl₄ were used, and only ethyl-branched polyethylene was obtained.

In this article, we report a tandem catalysis constituted of traditional Ziegler–Natta catalyst and 2,6-bis(imino)pyridyl iron complex to synthesize branched polyethylene with different branches from ethyl, butyl to hexyl, and even longer ones. The polymerization results and properties of branched polyethylene are discussed.

EXPERIMENTAL

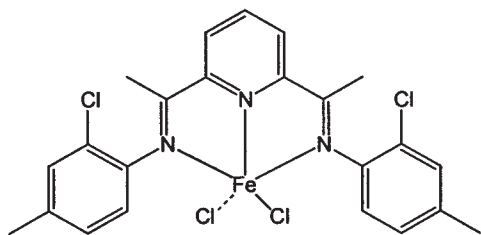
Materials

MAO solution (1.4 mol/L in toluene) was purchased from Albemarle Company (USA). The oligomerization catalyst (1), $\{[(2\text{-ArN}=\text{C}(\text{CH}_3))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ (Ar=2-Cl-4-CH₃-C₆H₃) (Scheme 1), was synthesized according

Correspondence to: Y. Hu (huyl@iccas.ac.cn).

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Scheme 1 Structure of iron complex 1.

to the method reported in the work done by Zhang et al.²² Polymerization-grade ethylene, TEA solution in heptane (1.8 mol/L) was 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.

Preparation of Ziegler–Natta catalyst ($\text{TiCl}_4/\text{MgCl}_2$) (2)

Ziegler–Natta catalyst ($\text{TiCl}_4/\text{MgCl}_2$) (2) (Ti = 4.77% in weight) was prepared by the following process:²³ A reactor equipped with a stirrer was purged with nitrogen 2–3 times. Tributylphosphate (0.1 mol) and dried magnesium chloride (0.05 mol) were added in it under stirring, and then the reaction temperature was increased to 80°C. After 2 h, the reaction system was obtained as semitransparent solution. Dried ethyl alcohol (0.03 mol) was added into the reaction system when the reaction temperature was decreased 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 remained was washed with 1,2-dichloroethane for three times and hexane for two times. Catalyst 2 ($\text{TiCl}_4/\text{MgCl}_2$) was obtained as brown yellow powder after the solid was dried under vacuum for more than 6 h at 50°C.

In situ polymerization of ethylene at atmospheric pressure

A 250-mL dried three-necked flask with a stirring bar was purged with dry nitrogen 2–3 times and then ethylene once. Then, 100 mL of toluene and a prescribed amount of TEA and MAO were injected in it, 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, 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 products were dried under vacuum for 6 h.

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 with 35°C (10 min), heated at 10°C/min to 220°C, and kept at 220°C for 10 min. ¹³C nuclear magnetic resonance (¹³C-NMR) analysis was performed on Bruker AM-300 operating at 120°C and 75 MHz. The polymer solutions were prepared in *o*-dichlorobenzene in a sample tube with diameter of 5 mm. The deuterated solvent was used to provide the internal lock signal. The chemical shifts were referenced internally to methylene carbon of main chain backbone resonance, which was taken as 30.00 ppm from Me_4Si . Spectra were taken with a 45° flip angle, an acquisition time of 0.983 s, and a delay of 3.0 s. The melting points (T_m) and the crystallinity of polymers were determined by differential scanning calorimetry (DSC) using a DSC 7A (Perkin–Elmer) operating at a heating rate of 10°C/min from 30 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.

RESULTS AND DISCUSSIONS

Ethylene oligomerization with iron catalysts

The 2,6-bis(imino)pyridyl iron complex 1, activated by MAO, exhibited high activity for ethylene oligomerization.²² The oligomers obtained were mainly α -olefins (>94%) and C_4 – C_{12} (>90%), which make this complex to be an excellent oligomerization catalyst. But it exhibited almost no catalytic activity when the sole TEA was used as cocatalyst because of chain-transfer reaction to the aluminum, which has been discussed in detail by Gibson.²⁴ Because TEA had to be used as cocatalyst when catalyst 2 was copolymerization catalyst in tandem catalyst system, the effect of TEA on the oligomerization of ethylene with this complex had also been investigated.

The oligomerization results of catalyst 1, activated by the mixture of TEA and MAO, were summarized in Table I. The catalytic activities decreased from 15.05×10^6 g/mol Fe h to 2.40×10^6 g/mol Fe h as reaction temperature was increased from 40 to 70°C, and changed little when more MAO was used. When more TEA was added, the catalytic activity decreased, but it was still as high as about 7×10^6 g C_2H_4 /mol Fe h. From 40 to 50% of total products were 1-butene and

TABLE I
Ethylene Oligomerization with 1/TEA/MAO

Run	TEA (mL)	MAO (mL)	Temp (°C)	Yield (g)	Activity 10 ⁶ g/mol Fe h	1-Butene (%)	1-Hexene (%)	≥1-Octene (%)	Total (%)
1	0.2	1	40	7.52	15.05	19.4	23.2	57.4	>94
2	0.2	1	50	4.87	9.75	23.9	23.8	52.3	>96
3	0.2	1	60	3.22	6.45	29.4	24.6	46.0	>96
4	0.2	1	70	1.20	2.40	30.4	24.6	45.0	>95
5	0.1	1	50	5.73	11.45				
2	0.2	1	50	4.87	9.75	23.9	23.8	52.3	>96
6	0.4	1	50	3.98	7.95				
7	0.6	1	50	3.87	7.74	24.6	23.7	51.7	>96
2	0.2	1	50	4.87	9.75	23.9	23.8	52.3	>96
8	0.2	2	50	5.05	10.10				
9	0.2	3	50	5.04	10.08	24.0	23.9	52.1	>95
10	0.2	4	50	5.03	10.07				

Reaction conditions: Fe = 1 μmol; reaction time = 30 min; ethylene pressure = 0.1 MPa; 50-mL toluene as solvent.

1-hexene, and the others were 1-octene and 1-alkenes with longer chains than 1-octene. As the reaction temperature was increased, the oligomers were shifted to lower-molecular-weight as shown in Figure 1. But the cocatalysts (MAO and TEA) exhibited less effect on the distribution of products. This made catalyst 1 suitable as one component for a tandem catalysts pair with 2 to prepare branched polyethylene with both short and long branches.

Ethylene polymerization with TiCl₄/MgCl₂

It was well-known that TiCl₄/MgCl₂ was traditionally activated by alkylaluminum. The results of catalyst 2/TEA used for ethylene polymerization at different conditions were summarized in Table II. The catalytic activities increased as the reaction temperature was increased. When polymerization temperature was kept at 50°C, the activities reached maximum at

0.2-mL TEA. When some MAO was introduced, the catalytic activity was unchanged comparing with those obtained from sole TEA used as shown in Table II. That meant there was not an adverse reaction between MAO and catalyst 2, which makes it possible to combine 1 and 2 together as tandem catalysts pair.

In situ polymerization of ethylene with tandem catalysts system of TiCl₄/MgCl₂ and iron catalyst

The ethylene polymerization with tandem catalysts system of 1/2, mixture of TEA and MAO as cocatalysts, was investigated and the results were summarized in Table III. 1-Alkenes were produced by catalyst 1/MAO and then copolymerized with ethylene to prepare branched polyethylene by catalyst 2/MAO as described in Scheme 2. The presence of 1 resulted in an increase in catalytic activity of all the reactions, which was always called a comonomer effect. The *T_m* and *X_c* of polymers obtained from 1/2 (Run 2, 4, and 7 in Table III) was lower than that obtained from catalyst 2 alone (Run 9, 11, and 14 in Table II), which indicated the products were branched polyethylene. In addition, the copolymerization of 1-olefins with ethylene had also led to the lower molecular weight and wider molecular weight distribution of polymer. (Run 2, 4, and 7 in Table III corresponding to run 9, 11, and 14 in Table II, respectively).

The molar ratio of the two catalysts exhibited obvious effect on the polymerization of ethylene and the properties of products. At a fixed amount of 2 (12 μmol), an increase of 1 (from 0.5 to 2.0 μmol) led to a maximum catalytic activity at 1.0 μmol catalyst 1 used (Table III, Run 8–10). More comonomers would be incorporated into the backbone chain when more oligomerization catalyst was introduced into the reaction system, and as a result, the catalytic activities were increased. But, too many comonomers could inhibit ethylene monomer to incorporate the active sites and

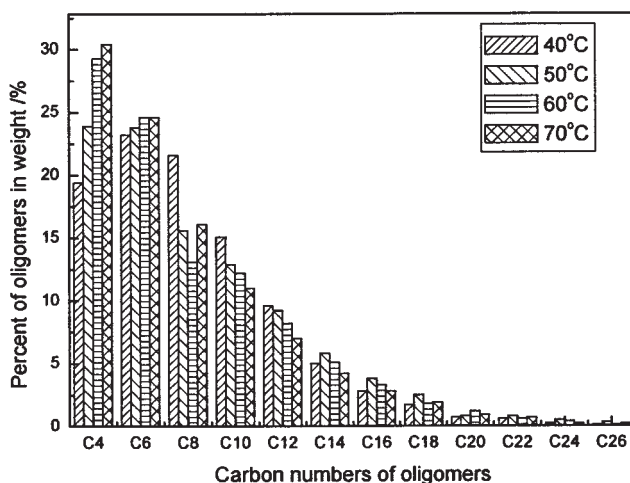


Figure 1 The effect of MAO on the catalytic activity of catalyst 2.

TABLE II
Ethylene Polymerization with $\text{TiCl}_4/\text{MgCl}_2$ (2)

Run	TEA (mL)	MAO (mL)	Temp (°C)	Yield (g)	Activity 10^6 g/mol Ti h	T_m (°C)	X_c (%)	M_w	M_w/M_n
1	0.4	0	40	7.5	1.25				
2	0.4	0	50	8.81	1.47	132.0	63.5		
3	0.4	0	60	9.84	1.64				
4	0.4	0	70	10.2	1.70				
5	0.1	0	50	9.18	1.53				
6	0.2	0	50	9.78	1.63				
3	0.4	0	50	8.81	1.47				
7	0.8	0	50	8.81	1.47				
8	0.1	2	50	8.43	1.41				
9	0.2	2	50	7.71	1.29	133.1	54.0	983700	5.49
10	0.4	2	50	7.49	1.25				
11	0.6	2	50	9.13	1.52	133.4	55.2	842500	7.04
12	0.2	1	50	8.88	1.48				
9	0.2	2	50	7.71	1.29	133.1	54.0	983700	5.49
13	0.2	3	50	8.83	1.47				
14	0.2	4	50	8.55	1.43	133.7	56.3	729900	8.76

Reaction conditions: Ti = 12 μmol ; reaction time = 30 min; ethylene pressure = 0.1 MPa; 50-mL toluene as solvent; TEA as cocatalysts.

made the copolymerization activity decrease. The results that branching degrees increased from 14/1000C (Run 2) to 29/1000C (Run 10) and T_m and X_c decreased significantly indicated that more comonomers were incorporated into the growing chain when the amount of 1 was increased as shown in Table III. There was an optimal Fe/Ti molar ratio for high-catalytic activity at the same reaction conditions. In addition, the acceleration of β -H elimination due to the insertion of comonomers also resulted in a decrease of the molecular weight, as shown in Table III.

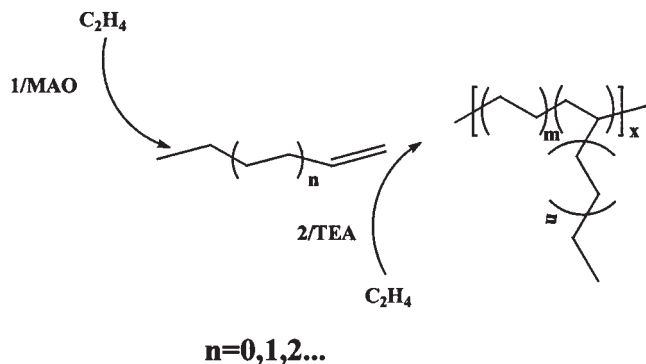
The catalytic activities of tandem catalytic system exhibited some increase when more TEA was used, as shown in Table III (Run 1–4), which could be attrib-

uted to the effects of TEA on two catalysts and comonomer effect, respectively. The branching degrees and thermal properties of polyethylene obtained showed that less comonomers was incorporated into the growing chain, which was caused by the decrease of oligomerization activities due to the introduction of TEA. The molecular weight of polymer was enhanced, accordingly. Compared with TEA, MAO showed less influence on the tandem reaction activities in the presence of 0.2-mL TEA, and so did the properties of resulting products as shown in Table III. This could be attributed to the less effect of MAO on the catalytic activities of catalyst 1 and 2, respectively, which was well accordance with the results discussed earlier.

TABLE III
Ethylene Polymerization with Tandem Catalyst System (TEA and MAO as cocatalysts)

Run	Fe (μmol)	Temp (°C)	MAO (mL)	TEA (mL)	Yield (g)	Activity (10^6 g/mol Ti h)	T_m (°C)	X_c (%)	Branching (C/1000)	M_w (M_w/M_n)
1	1	50	2	0.1	9.44	1.57	122.7	27.9		
2	1	50	2	0.2	11.22	1.87	123.4	31.8	14	543,800 (9.0)
3	1	50	2	0.4	11.40	1.90	123.6	34.2		
4	1	50	2	0.6	11.70	1.95	125.8	37.5	8	700,600 (12.1)
5	1	50	1	0.2	10.05	1.68	122.4	31.0		
2	1	50	2	0.2	11.22	1.87	123.4	31.8	14	543,800 (9.0)
6	1	50	3	0.2	11.40	1.90	123.4	32.4		
7	1	50	4	0.2	11.50	1.92	122.8	31.3	16	458,500 (8.8)
8	0.5	50	2	0.2	10.99	1.83	125.1	37.2		
2	1	50	2	0.2	11.22	1.87	123.4	31.8	14	543,800 (9.0)
9	1.5	50	2	0.2	10.04	1.67	123.7	26.9		
10	2	50	2	0.2	8.00	1.33	122.4	25.4	29	436,700 (8.1)
11	1	40	2	0.2	9.03	1.51	120.5	19.0		
2	1	50	2	0.2	11.22	1.87	123.4	31.8	14	543,800 (9.0)
12	1	60	2	0.2	10.82	1.80	128.0	42.9		
13	1	70	2	0.2	7.10	1.18	129.2	48.4	8	366,700 (11.4)

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



Scheme 2 *In situ* copolymerization of ethylene with iron and Z-N catalysts.

Among the reaction conditions, the reaction temperature played an important role on the catalytic activities and properties of products. The catalytic activities of 1/MAO/2/TEA increased to maximum and then decreased as reaction temperature was increased from 40 to 70°C. As discussed earlier, the increase of reaction temperature resulted in rapid decrease of oligomerization activity and some decrease of polymerization activity at 70°C. The trend of tandem reaction activities could be accounted for by combining the effects of reaction temperature on comonomers concentration and the polymerization activities together. The results that branching degrees were decreased and T_m and X_c of products were increased indicated

that the decrease of comonomers concentration was the main reason.

Characterization of branched polyethylene

The branching degrees of resulting polymers were measured from ^{13}C -NMR and the ^{13}C -NMR spectrum of branched polyethylene obtained when $\text{Fe} = 1 \mu\text{mol}$, $\text{Ti} = 12 \mu\text{mol}$, 0.2 mL TEA, and 2 mL MAO as cocatalysts, 0.1 MPa ethylene pressure at 50°C was presented in Figure 2. According to Galland et al.,²⁵ the presence of ethyl branches ($n = 0$) is confirmed by resonance at $\delta = 11.17, 26.73,$ and 39.71 ppm and butyl branches ($n = 1$) at $\delta = 23.30$ ppm. The longer branches ($n \geq 2$) could be detected by the signal at $\delta = 14.09, 32.21,$ and 38.13 ppm. The ^{13}C -NMR spectrum shows that the obtained polymer is branched polyethylene with total branches from 8/1000C to 29/1000C, including ethyl, butyl, and longer branches. No signal of unreacted α -olefins is detected in the resulting polymer on the ^{13}C -NMR spectrum. The distribution of branches was also calculated according to Galland et al.,²⁵ and the results were listed in Table IV. Not only ethyl, butyl, but also hexyl and longer branches were detected in all the products. And, almost one third of branches of some sample (sample 4) were hexyl and longer branches. That indicated that the short- and long-chain branched polyethylene was obtained by this tandem catalysis.

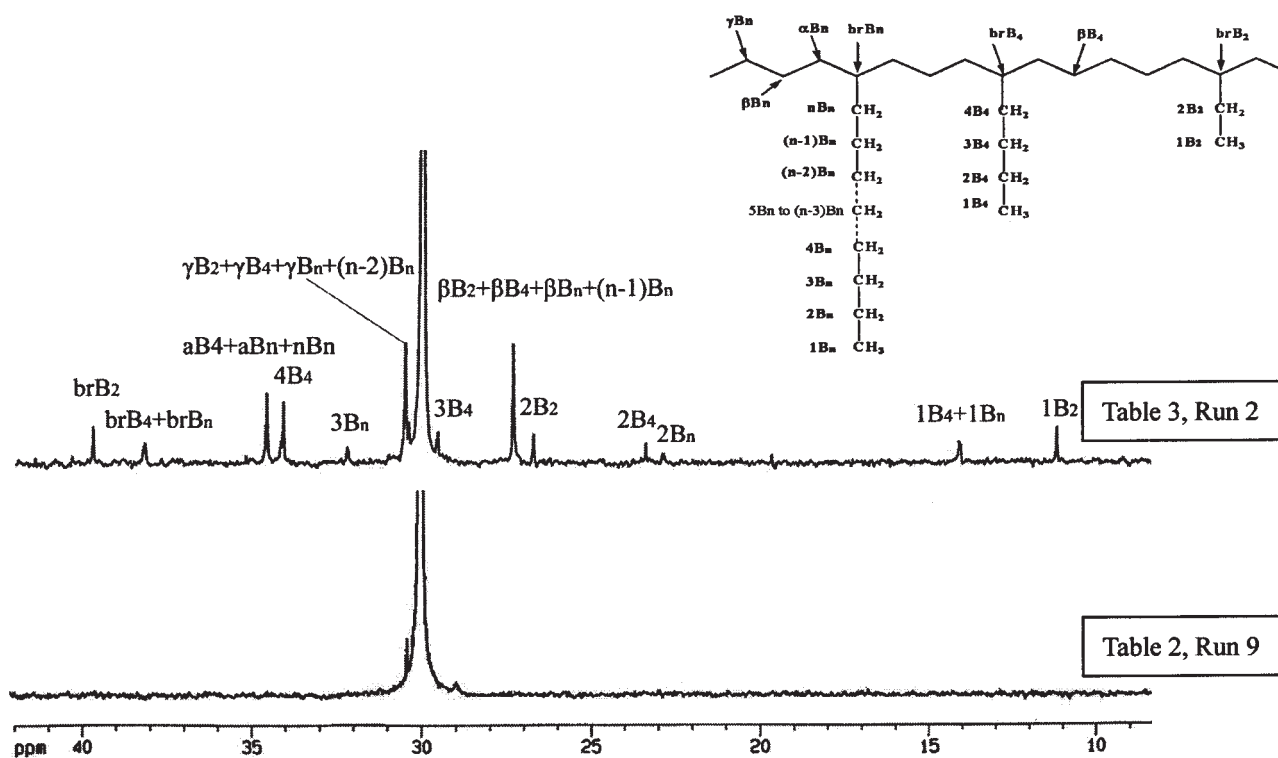


Figure 2 ^{13}C -NMR spectra of polyethylene obtained by tandem catalysts system (Table III, run 2) and Ziegler-Natta catalyst (Table II, run 9).

TABLE IV
The branching degrees and distributions measured from ^{13}C NMR spectrum

Sample	Run	Fe μmol	Temp $^{\circ}\text{C}$	MAO mL	TEA mL	ethyl	Branching C/1000 butyl	\geq hexyl	total
1	2	1.0	50	2	0.2	6.6	3.4	4.2	14.2
2	4	1.0	50	2	0.6	4.7	2.2	1.5	8.4
3	7	1.0	50	4	0.2	8.6	4.3	2.6	15.5
4	10	2.0	50	2	0.2	13.6	5.6	9.8	29.0
5	13	1.0	70	2	0.2	4.5	2.3	1.4	8.3

The molecular weights and distributions of the products were measured by GPC curves. The GPC curves of products (Run 2 and 4) exhibited broad unimodal ($M_w/M_n = 9.0$ and 12.1) as shown in Figure 3. The molecular weights and distributions of polymers were much higher than those obtained from metallocene^{7,12,17,18} as copolymerization catalysts in the same procedure, which would provide better mechanical properties and processability for the products.

CONCLUSIONS

In general, a 2,6-bis(imino)pyridyl iron catalyst and traditional Ziegler–Natta catalyst were combined together as tandem catalysts for *in situ* polymerization of ethylene. A series of branched polyethylene with different branches from ethyl, butyl to hexyl, and longer ones were produced. The alteration of comonomer concentration in reaction system resulted in the different catalytic activities and then the different product properties. The products obtained exhibited higher molecular weight and broader molecular weight distribution than those obtained from metallocene as copolymerization catalysts of tandem catalysis.

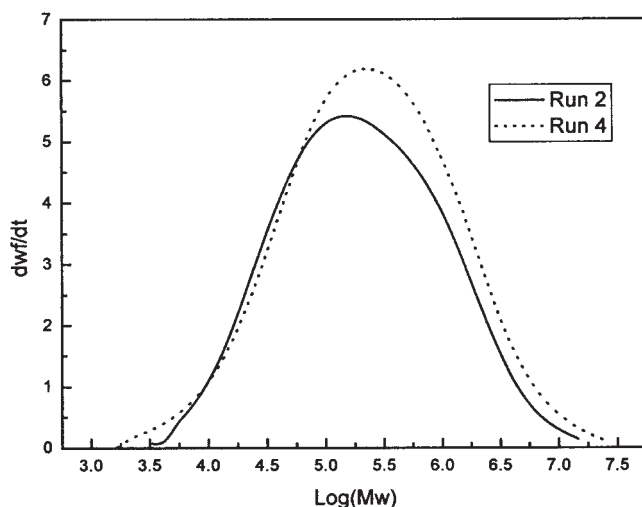


Figure 3 GPC curves of polyethylene obtained by tandem catalysts system (Table III, run 2 and 4).

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