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Preparation of Linear Low-Density Polyethylene by *In Situ* Copolymerization of Ethylene with Zr Supported on Montmorillonite/Fe/Methylaluminoxane Catalyst System

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ABSTRACT: Linear low-density polyethylene (LLDPE) was prepared by *in situ* copolymerization of ethylene with dual-functional catalysts that were composed of *rac*-Et(Ind)₂ZrCl₂ supported on montmorillonite (MMT) and $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ [Ar = 2,4-C₆H₄(Me)₂] oligomerization catalyst. A series of polyethylenes with different degrees of branching were obtained by adjusting the ratio of Fe and Zr (Fe/Zr). DSC, NMR, GPC, SEM, and density-gradient method were used to characterize the polymers. With increasing Fe/Zr ratio, the densities and melting points of polymers decreased, whereas the branching de-

grees and molecular weights increased. When the Fe/Zr ratio was increased, the activities of the catalysts decreased at atmospheric pressure and increased at 0.7 MPa ethylene pressure. SEM micrographs revealed that the morphology of branched polyethylene, produced with the catalyst supported on MMT, is better than that produced by the catalyst in a homogeneous system. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1690–1696, 2004

Key words: copolymerization; linear low-density polyethylene (LLDPE); oligomers; branched; catalysts

INTRODUCTION

In situ copolymerization of ethylene is a novel method of synthesizing linear low-density polyethylene (LLDPE), by using a single-feed ethylene and two catalysts in a single reactor—also called tandem reaction—and first reported by Beach and Kission^{1,2} in 1984 and 1986. Ethylene is oligomerized to oligomers with one catalyst, and copolymerized with the obtained oligomers to produce LLDPE with another catalyst. After that, the different combinations^{3–8} of oligomerization catalysts and polymerization catalysts were subsequently investigated. Unfortunately, their application was limited by poor catalyst compatibility, the instability of catalysts because of the interference of catalysts and cocatalysts, and poor selectivity for α -olefins.

The invention of a late-transition metal catalyst with high activity and selectivity for α -olefins seems to provide a series of perfect oligomerization catalysts. Bazan et al.⁹ synthesized branched polyethylene from ethylene by tandem reaction of iron and

zirconium single-site catalysts. Because methylaluminoxane (MAO) is the only cocatalyst used, there is no instability of catalysts in the reaction system. A series of polyethylenes with different branches and properties could be synthesized by adjusting the ratio of oligomerization catalyst and copolymerization catalyst. At the same time, they used other single-site catalysts^{10,11} to successfully prepare LLDPE in this procedure. Our group also carried out some work to produce LLDPE by *in situ* copolymerization.^{12,13}

Homogeneous polymerization, however, always causes some problems, such as the difficulty of cleaning the reactor, the initial activity is too high, and the activity falls too rapidly in their kinetics curve. The best method of solving these problems is supporting polymerization catalysts on some carriers, such as silica and MgCl₂, for example. Little has been reported thus far about montmorillonite (MMT) as a supporting catalyst. Recently, we developed a novel kind of supported catalysts, composed of *rac*-Et(Ind)₂ZrCl₂ supported on montmorillonite as polymerization catalyst and $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ [Ar = 2,4-C₆H₄(Me)₂] as oligomerization catalyst. This dual-functional catalyst was used *in situ* copolymerization to prepare a series of LLDPE with good morphology, having different degrees of branching and properties, in the present study.

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EXPERIMENTAL

Materials

rac-Et(Ind)₂ZrCl₂ and methylaluminoxane (MAO, 1.4 mol/L) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Albemarle Co. (Richmond, VA), respectively. Ethylene was of polymerization grade. Toluene was distilled from sodium/benzophenone and degassed. All other chemicals were obtained commercially and used as received. $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ [Ar = 2,4-C₆H₄(Me)₂] was synthesized according to the method in Britovsek et al.¹⁴

Preparation of MMT supported ethylene copolymerization catalyst

To a 250-mL dried three-neck flask, with a stirring bar, 4 g of MMT and 20 mL of MAO were added, stirred, and reacted at 50°C for 8 h. After removing the solvent and unreacted MAO, the solution of 0.5 g *rac*-Et(Ind)₂ZrCl₂ in toluene was added, stirred, and reacted at 50°C for 8 h under the same conditions as mentioned above. The unsupported *rac*-Et(Ind)₂ZrCl₂ was removed by washing with toluene and drying under vacuum at 50°C, after which an MMT-supported ethylene copolymerization catalyst with Zr loading 200 μmol/g, based on the total weight of the immobilized catalyst, was obtained.

In situ polymerization of ethylene at atmospheric pressure

A 250-mL dried three-neck flask, with a stirring bar, was purged with dry nitrogen two to three times and then once with ethylene, after which 100 mL of toluene and a prescribed amount of MAO were injected into the mixture and magnetically stirred at 60°C. Ethylene monomer was continuously charged to the flask and its pressure was maintained at 0.1 MPa by an electronic-magnetic valve; 2 min later, MMT-supported copolymerization catalyst and the solution of oligomerization catalyst were added to the reactor and *in situ* polymerization started. The polymerization was terminated by the addition of 10 wt % acidified ethanol and the resulting material was dried under vacuum.

The procedure of ethylene oligomerization at atmospheric pressure was carried out under conditions identical to those mentioned above; the difference consisted in adding the solution of oligomerization catalyst alone to the reactor.

In situ polymerization of ethylene in autoclave

After a stirred 2-L reaction vessel was back-filled with dry nitrogen several times and then once with ethylene at 70°C, 1 L toluene and a certain amount of MAO were injected sequentially into the reaction vessel.

After 2 min, the oligomerization catalyst and MMT-supported copolymerization catalyst were added simultaneously to the reaction vessel to start the *in situ* copolymerization. The ethylene pressure was maintained at 0.7 MPa during the polymerization. The polymerization was terminated with 10 wt % acidified ethanol and the resulting LLDPE was dried overnight under vacuum at 60°C.

Characterization

The Zr content of MMT-supported catalyst was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Poemstja Co.). ¹³C-NMR analysis was performed on a Bruker AM-300 instrument (Bruker, Darmstadt, Germany) operating at 120°C and 75 MHz. The polymer solutions were prepared in *o*-dichlorobenzene in a sample tube (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 Me₄Si. 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 Cetus Instruments, Norwalk, CT) operating at a heating rate of 10°C min⁻¹ from 30 to 160°C; the *T*_m was determined in the second scan. The densities of polymers were measured by the density-gradient method at 25 ± 0.1°C, in which the solvent was a mixture of chloroform and heptane. Scanning electron microscopy (SEM) was carried out on a Hitachi S-570 apparatus (Hitachi, Osaka, Japan). Gel-permeation chromatography (GPC) was carried out on a Waters-300 instrument (Waters Associates, Milford, MA) at 140°C and 1.0 mL/min. 1,2,4-Trichlorobenzene was used as solvent.

RESULTS AND DISCUSSION

Kinetics curves of polymerization

Figure 1 shows the kinetics curves of ethylene homopolymerization with zirconium catalyst supported on MMT [Fig. 1(a)], *in situ* copolymerization of ethylene with Zr (supported on MMT) and Fe (Fe/Zr = 1/4) as dual-functional catalysts [Fig. 1(b)], and oligomerization of ethylene with Fe catalyst [Fig. 1(c)]. One observes that the homopolymerization activity with zirconium catalyst supported on MMT increases initially and reaches a maximum at 7 min and then gradually decreases. Compared with the homopolymerization with the unsupported zirconium catalyst,¹³ the activity is lower but smoother and easier to be controlled, thus making it suitable for industrial use.

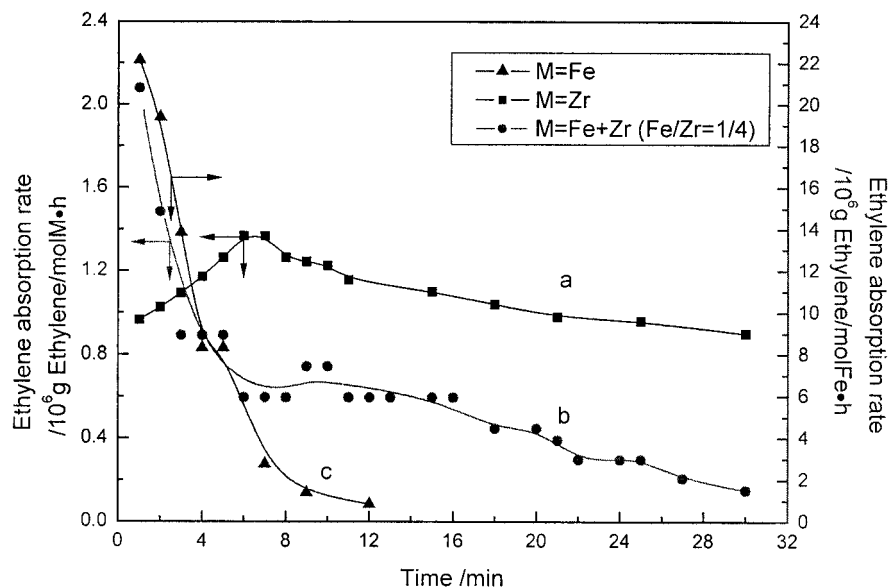


Figure 1 Kinetics curves of homopolymerization of ethylene with Zr catalyst (a), *in situ* copolymerization of ethylene with the ratio of Fe/Zr = 1/2 ($M = \text{Fe} + \text{Zr}$), and oligomerization of ethylene with Fe catalyst (b) (Zr catalyst is supported on MMT).

Note that it takes a longer period of time for the activity of supported zirconium catalyst to reach a maximum value because it needs some time to form active centers, arising from the migrations of MAO into the gallery space of MMT and its interlayer reactions with Zr catalyst. That means the presence of MMT is favorable to the stability of Zr catalyst. Additionally, it can be shown that the activity by *in situ* copolymerization of ethylene decreases rapidly within 4–5 min, maintained at about $0.6 \times 10^6 \text{ g mol}(\text{Fe} + \text{Zr})^{-1} \text{ h}^{-1}$ for about 10 min, after which it gradually decreases. This means that the introduction of oligomerization catalyst can obviously influence the kinetics curve of copolymerization. Clearly, the high activity at the beginning is mainly attributed to the oligomerization catalyst, which substantially agrees with the kinetics curve of oligomerization catalyst, and the activity after that is mainly attributed to the copolymerization catalyst. These phenomena imply that the two catalysts cannot interfere chemically with each other and exhibit respective catalytic characterization that contribute to the processes involved the migrations of MAO and oligomers into the gallery space of MMT and the interlayer reactions within it.

Activities of polymerization

In situ copolymerization of ethylene results are summarized in Table I. It can be seen that the activity of ethylene homopolymerization with *rac*-Et(Ind)₂ZrCl₂ supported on MMT is about $10^6 \text{ g mol}(\text{Zr})^{-1} \text{ h}^{-1}$ at atmospheric pressure and decreases somewhat by *in situ* copolymerization of ethylene. The amount of

MAO clearly influences the polymerization activities from Run 2 to Run 5, as shown in Table I. At the same Fe/Zr ratio, the polymerization activity is enhanced with increasing Al/(Fe + Zr) ratio and reaches a maximum when the Al/(Fe + Zr) ratio is 1000. Because it takes some time for MAO to diffuse into the gallery space of montmorillonite (i.e., the zirconium-based catalyst supported on MMT has much more time later to combine with MAO to generate active centers than does oligomerization catalyst in a homogeneous system as described above), when the concentration of MAO is lower, only a few copolymerization catalyst active centers are generated and take part in the polymerization so that the polymerization activity decreases. The higher concentration gradient of MAO around the MMT favors the diffusion of MAO in the MMT gallery and the generation of copolymerization active centers, when more MAO is introduced into the reaction system; this, in turn, allows the polymerization activities to increase. In addition, an increase in the MAO concentration will cause an increase in the rate of chain transfer to aluminum,¹⁴ and thus the activities of oligomerization and also *in situ* copolymerization are reduced because the concentration of MAO is too high.

It can also be found in Table I that by increasing the ratio of Fe/Zr, the polymerization activities decrease at atmospheric pressure (from Run 6 to Run 8). As reported in the literature,⁸ greater concentrations of late-transition metal oligomerization catalyst will produce a large amount of α -olefins, which causes the polymerization activities to decrease. In contrast, however, in the case of 0.7 MPa ethylene pressure, the

TABLE I
Data of *In Situ* Copolymerization of Ethylene to Prepare LLDPE

Run	Fe ^a (μ mol)	Zr ^b (μ mol)	Fe/Zr (mol/mol)	Al/(Fe + Zr)	Pressure (MPa)	A ^c	X ^d (%)	d ^e (g/cm ³)	T _m (°C)
1	0	7.6	0	1000	0.1	1.50	60.7	0.9578	133.9
2	1.82	7.3	1/4	250	0.1	0.20	22.0	0.9386	96.5
3	1.83	7.3	1/4	500	0.1	0.50	36.9	0.9387	113.3
4	1.75	7.0	1/4	1000	0.1	0.59	42.2	0.9418	117.7
5	1.62	6.5	1/4	2000	0.1	0.53	43.5	0.9420	118.0
6	0.55	6.6	1/12	1000	0.1	0.89	45.4	0.9514	122.3
7	0.87	6.9	1/8	1000	0.1	0.69	45.4	0.9478	120.9
4	1.75	7.0	1/4	1000	0.1	0.59	42.2	0.9418	117.7
8	2.0	4.0	1/2	1000	0.1	0.54	38.1	0.9384	114.5
9	0	17.3	0	1000	0.7	2.34	69.6	0.9650	131.1
10	1.7	20.3	1/12	1000	0.7	3.02	47.2	0.9386	121.4
11	1.2	9.0	1/8	1000	0.7	5.74	30.2	0.9364	98.9
12	5.0	20.0	1/4	1000	0.7	5.92	11.6	0.9282	86.2

Reaction conditions: temperature 60°C; reaction time: 30 min at atmospheric pressure, 60 min at 0.7 MPa ethylene pressure; cocatalyst: MAO.

^a Fe catalyst: $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ (Ar=2,4-C₆H₄(Me)₂).

^b *rac*-Et(Ind)₂ZrCl₂ supported on MMT.

^c Activity: 10⁶ g/mol (Fe + Zr) h.

^d Degree of crystallization.

^e Density.

polymerization activities increase as the ratio of Fe/Zr increases (from Run 9 to Run 12). Perhaps the β -H elimination reaction could be restrained at a higher pressure.¹⁵

Branching of polymers

A typical ¹³C-NMR spectrum of polyethylene, obtained with Fe/Zr ratio = 1/8 in the autoclave, is illustrated in Figure 2. According to Galland et al.,¹⁶

the presence of ethyl branches is confirmed by the resonance at $\delta = 10.94, 26.49$, and 39.47 ppm and butyl branches at $\delta = 22.94$ ppm. The longer branches ($n \geq 6$) can be detected by the signals at $\delta = 13.85, 31.93$, and 38.10 ppm. The signal of $\delta = 29.07$ ppm is attributed to the presence of α -olefins, which are not incorporated into the growing polyethylene chain. The ¹³C-NMR spectra show that the resulting products are branched polyethylenes with different branched chains including ethyl, butyl, and longer chains. When

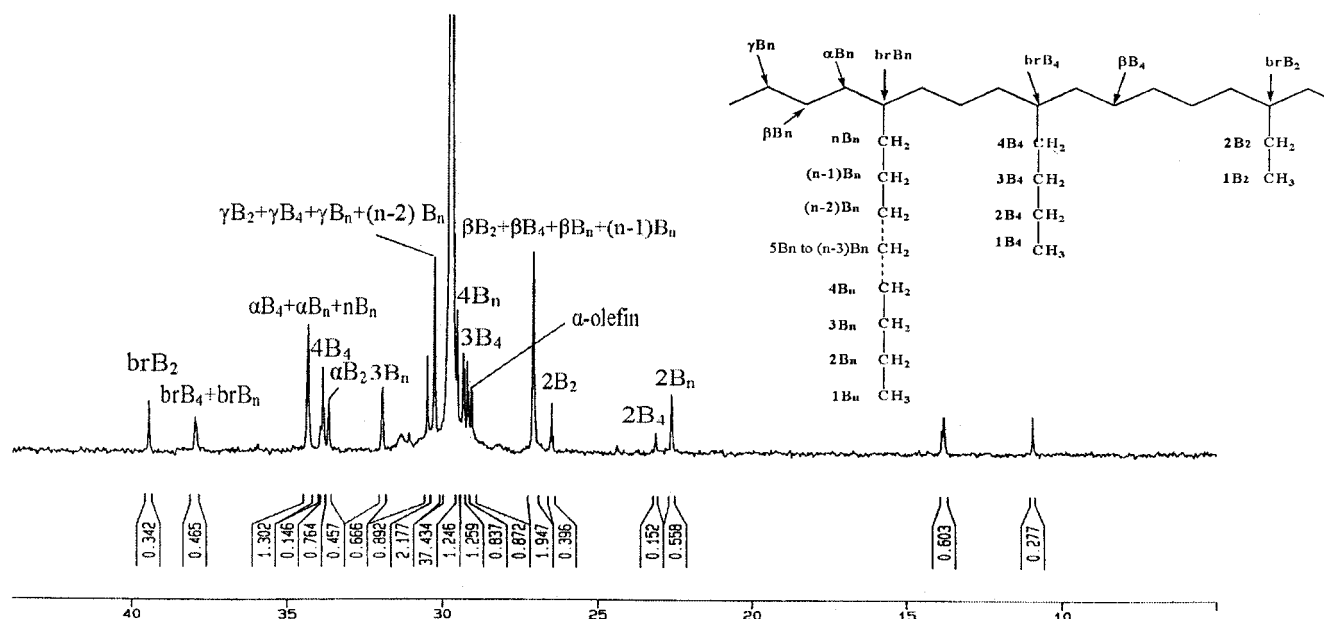


Figure 2 ¹³C-NMR spectrum of LLDPE prepared by *in situ* copolymerization of ethylene when Fe/Zr ratio is 1/8 (Run 11).

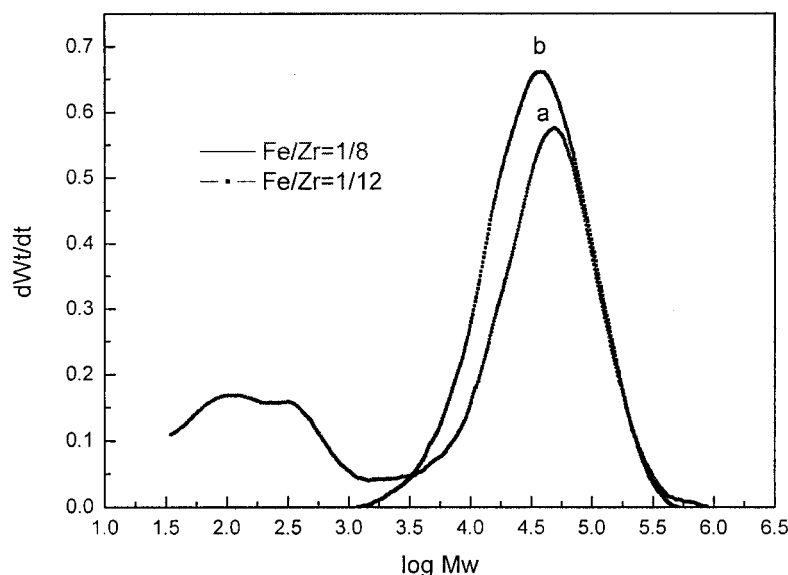


Figure 3 GPC chromatograph of LLDPE prepared by *in situ* copolymerization of ethylene when Fe/Zr ratio is 1/8 (a) and 1/12 (b).

the Fe/Zr ratio is 1/12, as shown in Figure 3, there are no oligomers to be observed in the final product, implying that most of oligomers produced have been incorporated into the copolymer. In some cases the presence of unreacted α -olefins is detected when high Fe/Zr ratios are used.

The branching degrees of polymers, the percentage of each type of branching (*i*) with respect to the total branches, N'_i , and of each type of branching with respect to the total ethylene units, N''_i , calculated from Galland et al.,¹⁶ are given in Table II, where *i* represents ethyl, butyl, and long branches, respectively. It can be found that the branching degrees increase from 24/1000°C to 78/1000°C when the Fe/Zr ratio increases from 1/12 to 1/4. A larger fraction of oligomerization catalyst will produce more α -olefins in the reaction system, which promotes greater incorporation of α -olefins into the growing polyethylene chain. At the same time, with respect to the total branching, the percentage of ethyl branches is invariable and the percentage of butyl branches increases, whereas the percentage of long branches decreases concomitantly with increasing Fe/Zr ratio. The results probably indicate that the copolymerization activity of

1-butylenes is unalterable and the copolymerization activity of 1-hexene increases when the concentration of comonomers increases.

Molecular weight and its distribution of LLDPE

GPC results of branched polyethylene obtained with the Fe/Zr ratio of 1/8 and 1/12 are shown in Figure 3(a) and (b), respectively. The distribution of molecular weight for the polymer obtained with the Fe/Zr ratio of 1/8 appears as a narrow one, centered at 63,407 (MW), and the other as a bimodal one with less than 1000 (MW). There is only one broader peak at 53,272 when the Fe/Zr ratio is 1/12. The molecular weight for the former is slightly higher than that for the latter as the amount of Fe catalyst increases. Also, the bimodal distribution of molecular weight [Fig. 3(b)] indicates the presence of unreacted α -olefins in the produced PE. It is interesting to note the bimodal distribution of MW, in which one is centered at about 110 and the other is centered at about 410: the first one corresponds to the α -olefins with about eight single-bonded C atoms and the second one corresponds to the α -olefins with about 28 single-bonded C atoms,

TABLE II
Amount of Branching in LLDPE

Run	Branching with respect to total			Branching with respect to the total [E] units				α -Olefin (%)	Branch (/1000°C)
	N'_E (%)	N'_B (%)	N'_L (%)	N''_E (%)	N''_B (%)	N''_L (%)	R (%)		
12	44.5	8.9	46.6	2.14	0.43	2.24	4.8	0	24.0
11	44.2	18.2	37.5	3.69	1.52	3.13	8.34	51.9	41.7
10	49.6	23.6	26.8	7.74	3.68	4.18	15.6	42.2	78.0

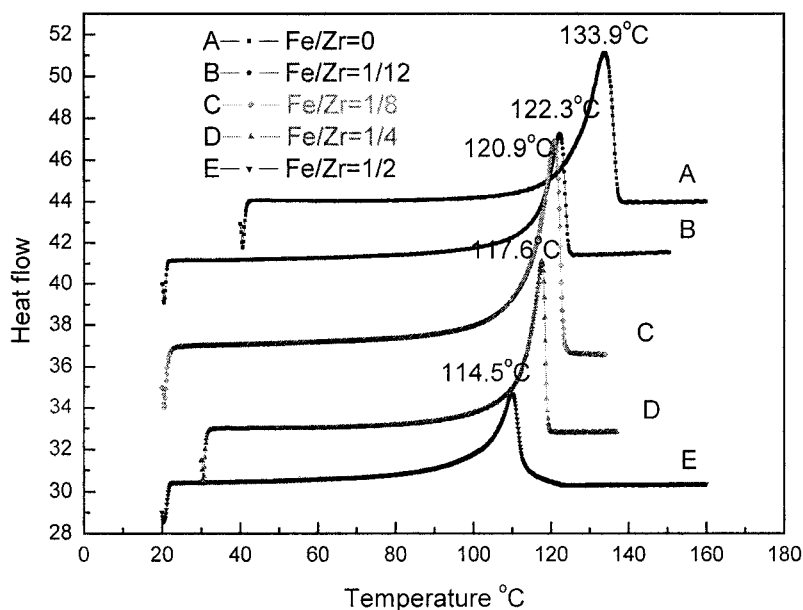


Figure 4 DSC curves of polyethylene samples prepared by the combined catalyst with different ratios of Fe/Zr.

given that the longer α -olefins are more difficult to incorporate into the growing polyethylene chain and remain in the PE products.

Thermal properties

DSC analysis reveals that the polymers obtained from different Fe/Zr ratios have different thermal properties. Figure 4 shows that all the polymers prepared under atmospheric pressure have only one peak and the melting points decrease from 133.9 to 114.5°C with increasing Fe/Zr ratio. Similarly, the crystallinity and/or the densities of polymers, prepared either under atmospheric or under high pressure, decrease (Table I). The greater the amount of comonomers incorporated into the growing polyethylene chain, the greater the number oligomerization catalysts added, especially under high pressure. Because the branched chains inhibit molecular-chain folding of PE into the growing crystal lamellae, it is difficult to form larger crystals in the system. Thus the degrees of crystallization, densities, and the melting point of polymers decrease as the Fe/Zr ratio increases.

The amounts of MAO introduced into the reaction system can also influence the thermal properties of polymers (Table I). The densities, melting points, and degrees of crystallization of the products increase as the amount of MAO increases. The branching degrees of LLDPE can be reduced with increasing concentration of MAO because the amounts of oligomers decrease as a result of chain transfer to Al, as reported in the literature.¹⁴

Morphology of polymers

SEM micrographs of polyethylene obtained by catalysts in a homogeneous system,¹⁷ supported on MMT, are shown in Figure 5. The microphotographs show an obvious difference between the polymers obtained from two kinds of catalyst systems. The morphology of polymers obtained from a homogeneous catalyst system is an agglomeration of loosely bounding flakes and has irregular shape, whereas the morphology of polymers obtained from catalyst supported on MMT is an agglomeration of closely bounding gross particles and has regular shape. Thus, the morphology of PE obtained from the catalyst supported on MMT is better than that from homogeneous catalyst system.

CONCLUSIONS

We prepared a series of LLDPE with good morphology and different properties by *in situ* copolymerization of ethylene with a dual-functional catalyst composed of *rac*-Et(Ind)₂ZrCl₂ supported on MMT and {[2-ArN=C(Me)₂C₅H₃N]FeCl₂} [Ar = 2,4-C₆H₄(Me)₂]. The branching degrees, densities, melting points, and molecular weights could be altered by adjusting the Fe/Zr ratio and the Al/(Fe + Zr) ratio. Results of GPC and ¹³C-NMR show that the branches of polymers can be increased by increasing the Fe/Zr ratio, although there will be more α -olefins that cannot be incorporated into the polyethylene chain and will thus remain in the polymers. In addition, the polymers' densities, melting points, and degrees of crystallization are affected by the amount of MAO by changing the oligomerization activ-

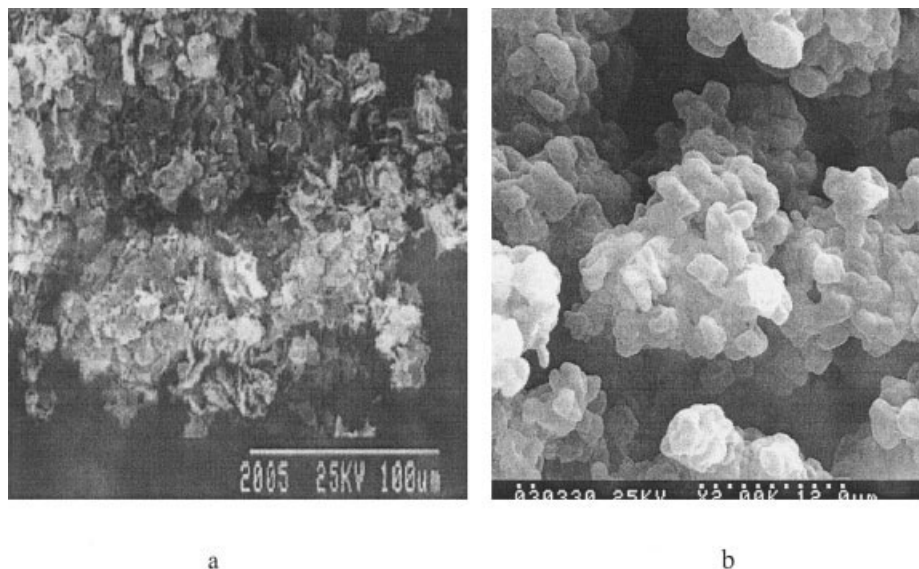


Figure 5 SEM micrographs of PE obtained from catalyst in homogeneous system (a)¹⁷ and polymerization catalyst supported on MMT (b) (Run 12) by *in situ* copolymerization.

ity and copolymerization activity. With increasing ethylene pressure, polymerization activities increase and the thermal properties of the obtained products decrease.

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