

Studies on the activation and polymerization mechanism of ethylene polymerization catalyzed by bis(imino)pyridyl iron(II) precatalyst with alkylaluminum

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Abstract

Different alkylaluminums (triethyl-, tri-*iso*-butyl-, *n*-trihexylaluminum) were tested as activator for the iron complex LFeCl₂ (**1**) (L = 2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine) in ethylene polymerization. Various polymerization temperatures and the molar ratios of Al/Fe prepared polyethylene (PE) with different molecular weights, molecular weight distributions, polymerization activities and polyethylene structures. Through the analysis of in situ UV–vis absorption spectra, ethylene polymerization results and prepared polyethylene structures, the distinctive behaviors of the catalytic system could result from a new applicable mechanism involving two different kinds of catalytic species LFeRCl (a) and LFeR₂ (b) (R = Et, *i*-Bu or He), the ratio of which varied with changing Al/Fe mole ratio when alkylaluminums were used as activators. The catalytic species (a) with very high activity mainly produced linear PE with high molecular weight in the bimodal PE. The catalytic species (b) with low activity mainly produced branched PE of low molecular weight in the bimodal PE.

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1. Introduction

Iron(II) complexes based on tridentate bis(imine)pyridine ligands and activated by methylaluminoxane (MAO) have been shown to be robust and extremely active catalysts for ethylene polymerization to form linear polyethylene [1–3]. Recently, it was reported that common alkylaluminum compounds, such as triethylaluminum (AlEt₃), tri-*iso*-butylaluminum (Al(*i*-Bu)₃) and so on, were also very effective in ethylene polymerization with a nickel-based complex [4]. The alkylaluminum compounds or aluminoxanes acted as chain transfer agents and therefore affected the molecular weights and molecular weight distributions of polymers [5–7]. However, the active species for

these iron(II) catalytic systems were not as well understood as those for the α -diimine nickel and palladium catalytic systems [8]. By analogy to Group 4 metallocene and the Group 10 metal systems, it was initially presumed that a 14-electron cationic Fe^{II} alkyl species was formed upon activation with MAO [5,9]. A number of theoretical studies were reported based on this assumption [10,11]. Neutral Fe^{II} complexes containing alkylaluminums in the coordination sphere of the metal have also been proposed [12,13]. EPR and Mössbauer studies revealed that the starting bis(imino)pyridine Fe^{II} complex was oxidized to an Fe^{III} species upon addition of MAO [14]. It was noteworthy that Fe^{II} and Fe^{III} precursors produced identical PE with similar activities, suggesting the presence of the same active species [5]. The precise nature of the active species remained undetermined in these catalytic systems.

In this paper, the homopolymerization of ethylene catalyzed with the complex LFeCl₂ (**1**) (L = 2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine) and AlR₃ (R = Et, *i*-Bu or He) was studied. It was found that polymerization temperature and the molar ratio of Al/Fe had large effect on the polymerization activities, molecular weights, molecular

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weight distributions and PE structures. The mechanism of the activation and polymerization was discussed.

2. Experimental

All operations and manipulations involving air- or moisture-sensitive compounds were carried out under a dry nitrogen atmosphere using glove box techniques. Hexane was refluxed over Na/benzophenone and distilled under nitrogen prior to use. Ethylene (polymer grade) was obtained from the Yanshan Petrochemical Corporation, China Petroleum & Chemical Corporation. Alkylaluminums (Witco) were used as received.

Polymerizations were carried out in a jacketed 1 L glass reactor (Büch Corporation) connected to a 5 L oil-bath (Huber Corporation). The reactor was purged with nitrogen and ethylene for three times, respectively. Then 500 mL of dry *n*-hexane was added into the reactor with stirring. At the same time, a prescribed amount of the catalyst solution in toluene was injected, followed by MAO or a hexane solution of AlEt₃, Al(*i*-Bu)₃ at room temperature. The polymerization temperature and the ethylene pressure were then set and maintained at the desired levels. After 30 min, the polymerization was terminated with ethanol containing 2% HCl. The resulting polymer was filtered and dried at room temperature until constant weight.

Melting points of the polymers were obtained on a Perkin-Elmer DSC-7 by heating from 0 °C to 160 °C at a heating rate of 10 °C/min. Weight-average (M_w), peak molecular weight (M_{pk}), molecular weight distribution (MWD) were measured by means of a Waters gel permeation chromatograph Alliance GPCV 2000 at 150 °C using 1,2,4-trichlorobenzene as the eluent. The in situ UV–vis spectroscopic experiments were completed in CH₂Cl₂ by using the Hp-8452A UV–vis spectrophotometer according to the general procedure of the published paper [9]. The crystallization analysis fractionation (CRYSTAF) was performed by a CRYSTAF apparatus, model 200, from Polymer Char S.A. (Valencia, Spain). The temperature was decreased at a rate of 0.2 °C/min from 160 °C to 30 °C. Fractions were taken automat-

ically and polymer concentration in solution was determined by an infrared detector using 3.5 μm as the measuring wavelength. ¹³C NMR spectra of PEs were recorded with a Bruker DMX 400 spectrometer operating at 100.6 MHz, on 10–20 mg/mL solutions in deuterated dichlorobenzene at 120 °C. Conditions: 5 mm probe; pulse repetition 4 s; numbers of scans 20,000.

3. Result and discussion

3.1. AlEt₃ as activator

3.1.1. Effect of the temperature and Al/Fe ratio in the ethylene polymerization

The results of ethylene polymerization with various temperatures and Al/Fe ratios were summarized in Table 1. As shown in entries (1–6), the catalytic system **1**/AlEt₃ was highly sensitive to the polymerization temperature. The activity increased greatly as the polymerization temperature rose from 5 °C to 25 °C. Then it decreased rapidly as the temperature rose from 25 °C to 65 °C. In the entry 2, the activity reached the maximum that was as high as 1.37×10^7 g PE/(mol Fe h) at 25 °C with Al/Fe ratio of 200. At high temperature, the low activity of the catalytic system possibly resulted from the deactivation of catalytic species. At the very low temperature, the low activity of the catalyst system might be involved in polymerization kinetics. The catalytic system had good activity in very narrow range of the polymerization temperature.

Besides the variations in polymerization activities with the polymerization temperature, changes in M_w s, M_{pk} s and MWDs of the prepared polymers could be observed. As shown in Fig. 1 and Table 1, unexpected result was bimodal PE. The nature of the MWD curves maintained a bimodal when the temperature was kept between 5 °C and 55 °C. However, the bimodal distribution changed greatly at different temperatures. With the polymerization temperature rising, the M_{pk} of the low molecular weight fraction (M_{pk1}) increased gradually from 474 to 776, while the M_{pk} of the high molecular weight fraction (M_{pk2}) decreased

Table 1
Ethylene polymerization catalyzed by complex **1** with AlEt₃

| Entry | Temperature (°C) | Al/Fe (mol/mol) | Activity ^a | $M_{pk} \times 10^{-3}$ (g/mol) ^b | | $M_w \times 10^{-5}$ (g/mol) ^b | MWD ^b | T_m (°C) ^c |
|----------------|------------------|-----------------|-----------------------|--|--------|---|------------------|-------------------------|
| | | | | Peak 1 | Peak 2 | | | |
| 1 | 5 | 200 | 7.35 | 0.645 | 174 | 2.76 | 62.7 | 134.7 |
| 2 | 25 | 200 | 13.7 | 0.474 | 70.1 | 1.78 | 39.7 | 133.0 |
| 3 | 35 | 200 | 12.1 | 0.547 | 53.7 | 1.67 | 29.5 | 132.9 |
| 4 | 45 | 200 | 1.61 | 0.658 | 39.7 | 0.432 | 32.2 | 129.2 |
| 5 | 55 | 200 | 0.316 | 0.776 | 23.6 | 0.507 | 40.2 | 128.5 |
| 6 | 65 | 200 | Very low | – | – | – | – | – |
| 7 ^d | 25 | 20 | 0.0675 | 0.298 | 214 | 4.04 | 22.3 | 135.2 |
| 8 | 25 | 500 | 20.6 | 0.463 | 81.2 | 1.63 | 29.4 | 132.9 |
| 9 | 25 | 2000 | 6.10 | 0.402 | 117 | 2.14 | 150 | 133.0 |
| 10 | 25 | 4000 | 0.644 | 0.238 | 147 | 1.83 | 209 | 132.5 |

General polymerization conditions: [Fe] = 1.07×10^{-5} M, $P = 1.0$ bar, $t = 30$ min, solvent: hexane.

^a In 10^6 g PE/(mol Fe h).

^b Determined by means of GPC.

^c Measured by means of DSC.

^d [Fe] = 1.0×10^{-4} M.

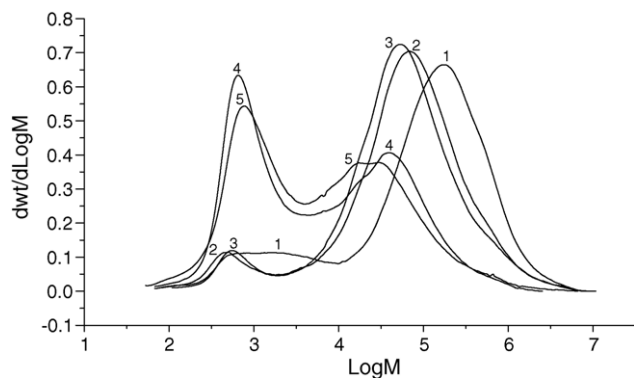


Fig. 1. GPC curves of PE prepared with catalytic system **1**/AlEt₃ at various temperatures: (1) $T=5^{\circ}\text{C}$, (2) $T=25^{\circ}\text{C}$, (3) $T=35^{\circ}\text{C}$, (4) $T=45^{\circ}\text{C}$ and (5) $T=55^{\circ}\text{C}$ (numbers of the curves correspond to entries in Table 1).

remarkably from 70,100 to 23,600. It seemed that the behavior was not consistent with the explanation that the alkylaluminum compounds or aluminoxane could accelerate chain transfer to aluminum at high temperature as chain transfer agents [3,5].

In addition, AlEt₃ was proved to be an effective activator in ethylene polymerization with Fe(II) complex. As the amount of AlEt₃ increased, the activity increased rapidly initially (entries 7, 2, 8), while it decreased sharply (entries 8–10). And the activity of the catalyst **1** using AlEt₃ as the activator was as high as $2.06 \times 10^7 \text{ g PE}/(\text{mol Fe h})$ at 25°C with Al/Fe ratio of 500 in the entry 8. At higher or lower Al/Fe ratio, the activity of the catalytic system was very low. The low activity of the catalytic system at low Al/Fe ratio might result from insufficient activation of the catalyst **1**. The higher Al/Fe ratio resulted in the decrease of the activity of the catalytic system, which might be due to the excessive deoxidization. On the basis of polymerization mechanism proposed by Gibson and co-workers [5], moderate increase of the AlEt₃ could maintain high activity of catalyst species and accelerate chain transfer to aluminum as a chain transfer agent which could lead to the changes in the M_w and MWD of prepared linear PE as observed. In Fig. 2, the most unexpected observation was with respect to the broad and bimodal MWD of polyethylene in the range of AlEt₃/Fe ratio from 20:1 to 4000:1. However, it was also reported by

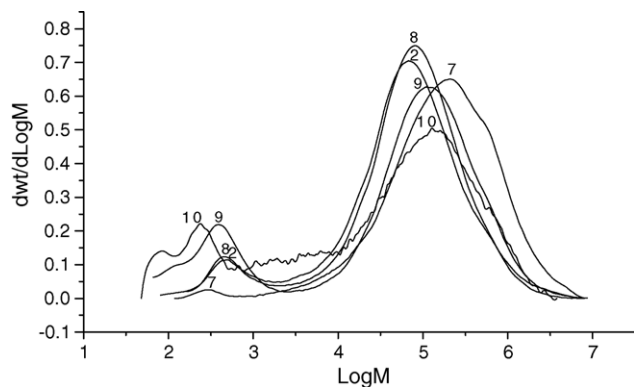


Fig. 2. GPC curves of PE prepared with catalytic system **1**/AlEt₃ at various Al/Fe molar ratios: (2) Al/Fe = 200, (7) Al/Fe = 20, (8) Al/Fe = 500, (9) Al/Fe = 2000 and (10) Al/Fe = 4000 (numbers of the curves correspond to entries in Table 1).

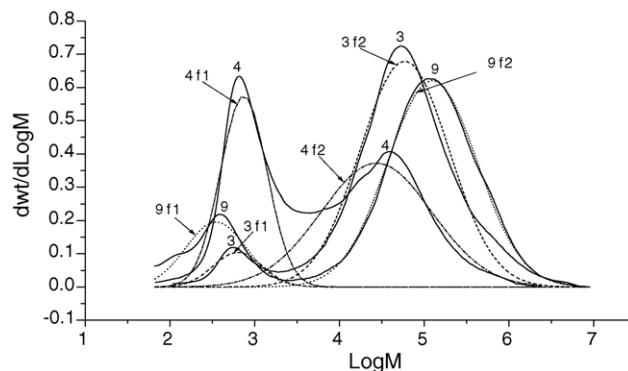


Fig. 3. The results of GPC curves fitting multi-peaks on Gaussian correspond to entries by using the Origin 6.0 soft package (numbers of the curves correspond to entries in Table 1).

Brookhart and co-workers [3] and Gibson and co-workers [5] that there was a broad bimodal with the similar catalyst only at appropriate Al/Fe ratio using MMAO or MAO as the activators, respectively. With the AlEt₃/Fe ratio increasing, the M_{pk1} decreased gradually from 474 to 238, while the M_{pk2} increased from 70,100 to 147,000, so that MWD increased rapidly. As the reported explanation [3,5], the M_{pk2} should decrease as well as the M_{pk1} because increasing of Al/Fe ratio accelerates chain transfer to aluminum and the MWD should be a unimodal at very high or low Al/Fe ratio. Moreover, chain transfer in the α -diimine catalytic system was quite slow relative to chain propagation because of the introduction of steric bulk in the axial sites of the square plane. Thus, high molecular weight polymer was produced. It seemed impossible that the low molecular weight fraction whose molecular weight was below 1000 resulted from the chain transfer in the catalytic system that produced the high molecular weight fraction from 20,000 to 140,000.

3.1.2. In situ UV–vis studies on the catalytic system **1**/AlEt₃

PE prepared with catalytic system **1**/AlEt₃ always had the broad and bimodal MWD and each peak seemed to be independent to some extent as seen in Fig. 3. In Table 2, each peak had a reasonable M_w/M_n (1.5–9.0) suggesting single site polymerization mechanism. The bimodal distribution changed greatly at different polymerization conditions. This observation was possibly consistent with the existence of two catalytic species whose ratios varied with changing Al/Fe ratios. As an alternative explanation for bimodal behavior, chain transfer to aluminum is a reasonable route for the formation of low molecular weight materials at the early stage of the polymerization [3]. As shown in Section 3.1.1, the changes of bimodal behavior in the catalytic system were not completely consistent with the explanation.

Moreover, two kinds of catalytic species in the catalytic system **1**/AlEt₃ were found by the in situ UV–vis spectroscopic experiments. In Fig. 4, complex **1** had absorption at 702 nm. After controlled amount of AlEt₃ was added, the absorption at 702 nm disappeared immediately. A new absorption at 570 nm grew up gradually when Al/Fe molar ratio was 40. Then addition of more amounts of TEA (Al/Fe = 4000) led to the separation at 570 nm into two absorption peaks at 568 nm and 586 nm. The two different and relative absorption peaks possibly represented

Table 2
The results of GPC curve analyses of PE prepared with catalytic system 1/AlEt₃

| Entry | Temperature (°C) | Al/Fe (mol/mol) | Activity ^a | Percentage (%) ^b | $M_{pk} \times 10^{-3}$ (g/mol) | | $M_w \times 10^{-4}$ (g/mol) | MWD | T_m (°C) |
|------------------|------------------|-----------------|-----------------------|-----------------------------|---------------------------------|--------|------------------------------|------|------------|
| | | | | | Peak 1 | Peak 2 | | | |
| 3 | 35 | 200 | 12.1 | – | 0.547 | 53.7 | 16.7 | 29.5 | 132.9 |
| 3f1 ^c | – | – | – | 9.88 | 0.620 | – | 0.0790 | 1.54 | – |
| 3f2 ^c | – | – | – | 89.82 | – | 60.6 | 12.2 | 4.30 | – |
| 4 | 45 | 200 | 1.61 | – | 0.658 | 39.7 | 4.32 | 32.2 | 129.2 |
| 4f1 ^c | – | – | – | 39.47 | 0.746 | – | 0.0905 | 1.49 | – |
| 4f2 ^c | – | – | – | 60.64 | – | 27.9 | 7.97 | 9.02 | – |
| 9 | 25 | 2000 | 6.10 | – | 0.402 | 117 | 2.14 | 150 | 133.0 |
| 9f1 | – | – | – | 17.69 | 0.349 | – | 0.0270 | 1.82 | – |
| 9f2 | – | – | – | 82.15 | – | 125 | 25.7 | 4.30 | – |

^a In 10⁶ g PE/(mol Fe h).

^b Percentage of each fitted peak area.

^c The result of fitting multi-peaks on Gaussian correspond to entries by using the Origin 6.0 soft package.

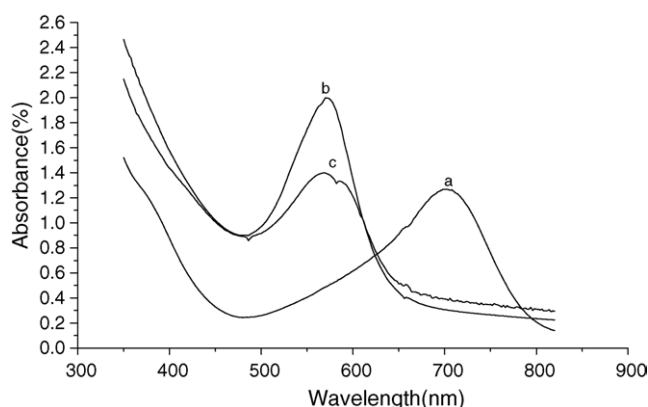
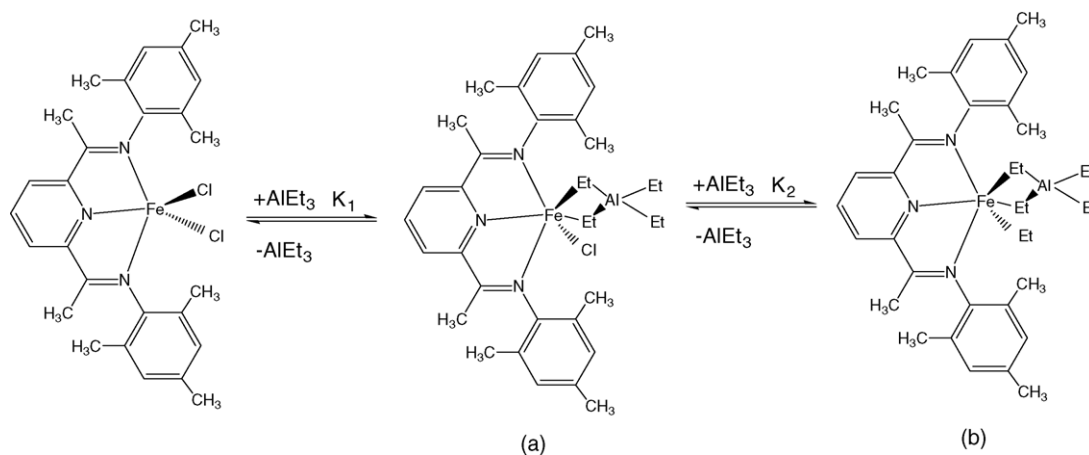


Fig. 4. In situ UV-vis absorption spectra for the catalytic system 1/AlEt₃ at various Al/Fe molar ratios in CH₂Cl₂ solvent: (a) complex 1, (b) Al/Fe = 40 and (c) Al/Fe = 4000.

two kinds of catalytic species. The catalytic species that had the absorption at 586 nm was clearly observed at very high Al/Fe molar ratio. The other catalytic species that had the absorption at about 570 nm always existed at low or high Al/Fe molar ratio. Maybe the ratios of the two catalytic species varied with changing Al/Fe ratios.

On the basis of the above results and discussions, for the bimodal behavior, the explanation of chain transfer via transmetalation is not perfect in the catalytic system. As an alternative explanation for the bimodal behavior, references [12,13,15] suggested the existence of two kinds of catalytic species whose ratios varied with changing Al/Fe ratio. When trialkylaluminum was used as activator in iron catalyst systems, two kinds of catalytic species were observed by ¹H NMR. In fact, there were probably several kinds of catalytic species in the Fe(II)/MAO system [12]. So it was possible that there were two different kinds of catalytic species (a and b) in the catalytic system as shown in Scheme 1. Based on the results that the ratios of Al/Fe and polymerization temperature had large effect on the activity, M_w , MWD and PE structures, two different kinds of catalytic species might give good explanations. When Al/Fe molar ratio was low, the catalytic species (a) possibly predominated in the catalytic system. However, the catalytic species (b) predominated at high Al/Fe molar ratio. The catalytic species (a) with possible absorption at 570 nm mainly resulted in the fraction of the high molecular weight. The catalytic species (b), which possibly had the absorption at 586 nm, mainly resulted in the fraction of the low molecular weight. Certain amount of AlEt₃ turned complex 1 into the catalytic species (a). And the UV-vis



Scheme 1. Proposed structures of catalytic species (a and b).

absorption band was converted into a new band at 570 nm from the initial peak located at 702 nm. As we know, the conjugated system can produce the $n \rightarrow \pi^*$ transition when the end group of the conjugated chain has unshared electron pairs, which leads to the red shift of the λ_{\max} . The ligand of the complex **1** was yellow. However, the prepared complex **1** was black blue after the ligand was chelated with FeCl_2 . The color change might result from the $n \rightarrow \pi^*$ transition of three unshared electron pairs in Fe cation. Under the function of the controlled AlEt_3 , the complex **1** turned into the catalytic species (a). The ethyl substituted one $-\text{Cl}$ group, which might decrease unshared electron pairs of Fe cation to two (seven outermost electrons). So the $n \rightarrow \pi^*$ transition was weakened and the λ_{\max} presented the blue shift from 702 nm to 570 nm. With addition of further amount of the AlEt_3 increasing, some of the catalytic species (a) were converted into the catalytic species (b). The ethyl further substituted the other $-\text{Cl}$, which might make electron saturation of Fe cation increase in the catalytic species (b). Then the $n \rightarrow \pi^*$ transition was strengthened and the λ_{\max} presented the red shift from 570 nm to 586 nm. This confirmed the early mentioned explanation for the bimodal behavior. Each catalytic species had independent polymerization behaviors such as chain propagation, chain transfer via transmetalation, chain termination and so on.

3.1.3. Structure characteristics of PE prepared with catalytic system **1**/ AlEt_3

The variations in the polymerization temperature and the amount of the AlEt_3 could also affect the structures of PE prepared by the catalytic system. As shown in Fig. 5, at high temperature, much more branched PE was produced compared with that at low temperature under the same conditions. There were three obvious peaks at 38.4 °C, 54.5 °C and 71.3 °C besides the main peak at 88.0 °C in the CRYSTAF curve of the entry 4, which represented four different kinds of PE chain structures [16,17]. Generally, the crystallization temperature of the branched polyethylene is lower than that of the linear polyethylene. So the main peak at 88.0 °C could be ascribed from the crystallization of the linear polyethylene and the other three

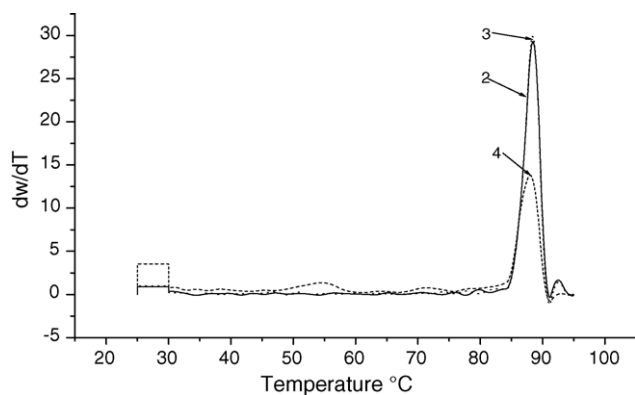


Fig. 5. CRYSTAF curves of PE prepared with catalytic system **1**/ AlEt_3 at various polymerization temperatures: (2) $T=25^\circ\text{C}$, (3) $T=35^\circ\text{C}$ and (4) $T=45^\circ\text{C}$ (numbers of the curves correspond to entries in Table 1).

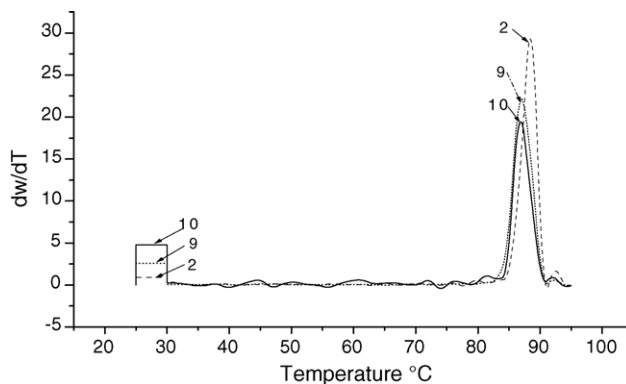


Fig. 6. CRYSTAF curves of PE prepared with catalytic system **1**/ AlEt_3 at various Al/Fe molar ratios: (2) Al/Fe=200, (9) Al/Fe=2000 and (10) Al/Fe=4000 (numbers of the curves correspond to entries in Table 1).

peaks could be the contribution from the crystallization of three different kinds of branched polyethylene. In the entry 4, the soluble fraction, which could not crystallize at 30 °C, was much more than that of the entries 2 and 3. And the linear polyethylene of the entry 4 was much less than that of the entries 2 and 3. In Fig. 6, PE prepared at various Al/Fe molar ratios had the similar character. The branched PE prepared at high Al/Fe molar ratio was much more than that at low Al/Fe molar ratio under the same conditions. There were three obvious peaks at 44.8 °C, 60.8 °C and 81.5 °C besides the main peak at 86.9 °C in the CRYSTAF curve of the entry 10. The soluble fraction at 30 °C gradually increased and the linear polyethylene gradually decreased with the Al/Fe molar ratio increasing. In addition, the crystallization temperature of the linear polyethylene decreased from 88.3 °C to 86.9 °C although the M_{pk2} increased with the Al/Fe molar ratio increasing. Consequently, it was possible that the linear polyethylene chains had a few branches with the Al/Fe molar ratio increasing, which led to the decrease of their crystallization temperatures.

To further confirm the PE structures, the ^{13}C NMR analyses were conducted as shown in Fig. 7. Besides isolated methylene carbons at 30.0 ppm, the entry 3 had least saturated end group carbons at 14.0 ppm, 22.8 ppm, 32.2 ppm and other carbons with different chemical shifts. As could be seen, PE from the entry 3 contained less branch and fraction of the low molecular weight than the entries 4 and 10. So the bimodal PE prepared with catalytic system **1**/ AlEt_3 was made up of linear polyethylene chains and a few branched polyethylene chains. And branched polyethylene chains mainly concentrated on the part of low molecular weight.

Fe(II) catalysts produce linear polyethylene with broad molecular weight distribution as well known. It was difficult to elucidate the reason that both the branched PE and linear one were produced in a single site catalytic system. It seemed reasonable that the changes in the PE structure might result from the effect of high temperature and Al/Fe molar ratio on the ratios and polymerization behaviors of the two kinds of catalytic species. The catalytic species (a) mainly produced linear PE with high molecular weight and the catalytic species (b) mainly produced branched PE with low molecular weight.

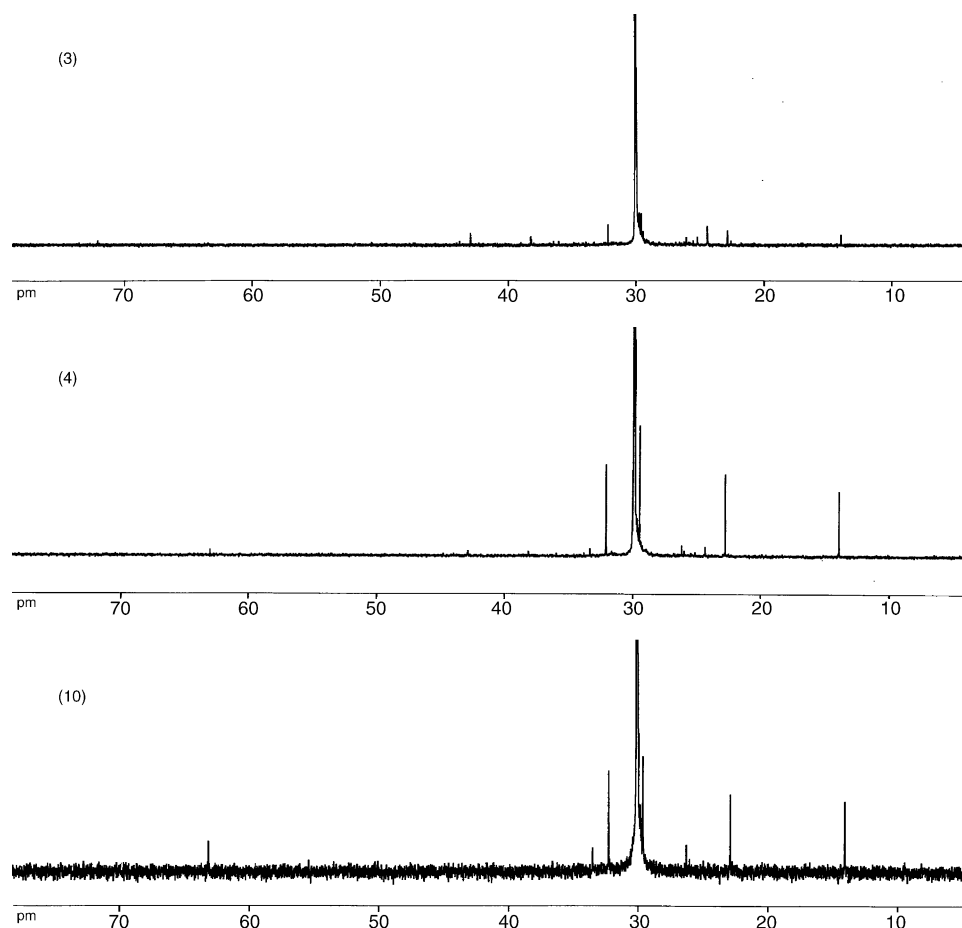


Fig. 7. ^{13}C NMR curves of PE prepared with catalytic system **1**/AlEt₃: (3) $T = 35^\circ\text{C}$, Al/Fe = 200; (4) $T = 45^\circ\text{C}$, Al/Fe = 200; (10) $T = 25^\circ\text{C}$, Al/Fe = 4000 (numbers of the curves correspond to entries in Table 1).

3.1.4. Effect of the polymerization time

The results of ethylene polymerization with catalytic system **1**/AlEt₃ at various polymerization times are summarized in Table 3. Obviously, the activity of the catalytic system was very high during the initial polymerization stage. It decreased gradually with the polymerization time prolonging. And the molecular structure of the PE changed greatly at the different polymeriza-

tion time. As can be seen in Fig. 8, the low molecular weight PE was mainly produced in the early polymerization stage. Especially, the amount of the low molecular weight PE was almost equal to the high molecular weight PE in the entry 17. The percentage of the low molecular weight PE decreased with the polymerization time increasing. When Al/Fe ratio was 1000, the M_{pk1} decreased and the M_{pk2} increased with the polymerization

Table 3
Ethylene polymerization catalyzed by **1**/AlEt₃ at various polymerization time

| Entry | Time (min) | Al/Fe (mol/mol) | Activity ^a | $M_{pk} \times 10^{-3b}$ (g/mol) | | $M_n \times 10^{-5b}$ (g/mol) | MWD ^b | T_m^c ($^\circ\text{C}$) |
|-----------------|------------|-----------------|-----------------------|----------------------------------|--------|-------------------------------|------------------|------------------------------|
| | | | | Peak 1 | Peak 2 | | | |
| 11 ^d | 30.0 | 200 | 13.7 | 0.463 | 68.5 | 4.48 | 39.7 | 133.0 |
| 12 | 5.0 | 200 | 33.7 | 0.474 | 59.1 | 3.08 | 37.8 | 132.7 |
| 13 | 2.5 | 200 | 43.1 | 0.486 | 71.8 | 2.81 | 54.2 | – |
| 14 | 1.0 | 200 | 40.1 | 0.570 | 65.0 | 1.81 | 56.5 | 130.9 |
| 15 ^d | 30.0 | 1000 | 16.5 | 0.392 | 85.6 | 1.71 | 88.2 | – |
| 16 ^e | 5.0 | 1000 | 132.3 | 0.523 | 73.1 | 4.30 | 39.5 | 133.5 |
| 17 ^e | 1.0 | 1000 | 177.9 | 0.628 | 71.2 | 1.58 | 61.4 | 131.5 |

General polymerization conditions: $[\text{Fe}] = 1.0 \times 10^{-5}$ M, $P = 1.0$ bar, $T = 25^\circ\text{C}$, solvent: hexane.

^a In 10^6 g PE/(mol Fe h).

^b Determined by means of GPC.

^c Measured by means of DSC.

^d $[\text{Fe}] = 1.07 \times 10^{-5}$ M.

^e $[\text{Fe}] = 0.2 \times 10^{-5}$ M.

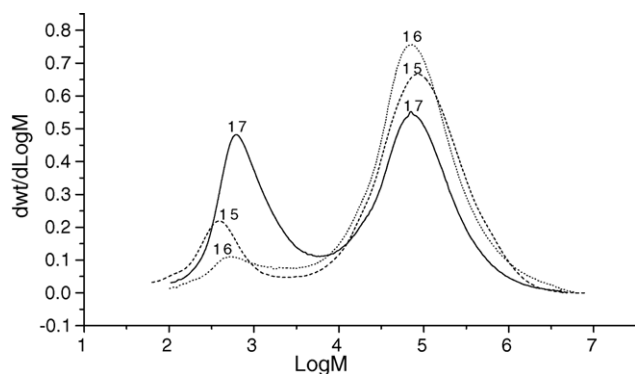


Fig. 8. GPC curves of PE prepared with catalytic system **1**/AlEt₃ at various polymerization time: (15) *t* = 30.0 min, (16) *t* = 5.0 min and (17) *t* = 1.0 min (numbers of the curves correspond to entries in Table 3).

time prolonging. It was obvious that the low molecular weight PE did not result from chain transfer via transmetalation of the catalytic species that could produce the high molecular weight PE. At the initial polymerization stage, there were many catalytic species (b) due to the high Al/Fe ratio. The catalytic species (b) mainly produced the low molecular weight PE. At the same time, there were a lot of catalytic species (a) that mainly produced the high molecular weight PE. Two kinds of catalytic species might have chain transfer via alkylaluminum. The catalytic species (a) were primary as the amount of AlEt₃ decreasing. So the catalytic system mainly produced the high molecular weight PE after the initial polymerization stage. It was well explained that the bimodal behaviors of the catalytic system changed as seen in Fig. 8.

3.2. Effect of different alkylaluminums

Furthermore, the catalytic systems **1**/Al(*i*-Bu)₃ and **1**/AlHe₃ had similar bimodal behaviors as **1**/AlEt₃ shown in Table 4 and Fig. 9. Every catalytic system had similar activities, bimodal behaviors and polymer structures. These catalytic systems possibly had the same activation and polymerization mechanism that there were two different kinds of catalytic species. However, catalytic system **1**/AlEt₂Cl had no activity in the ethylene polymerization. The *M*_{pk2} and MWD of PE prepared with the catalytic systems increased limitedly with alkyl bulk of alkylaluminums increasing from AlEt₃ to AlHe₃. Larger alkyl bulk

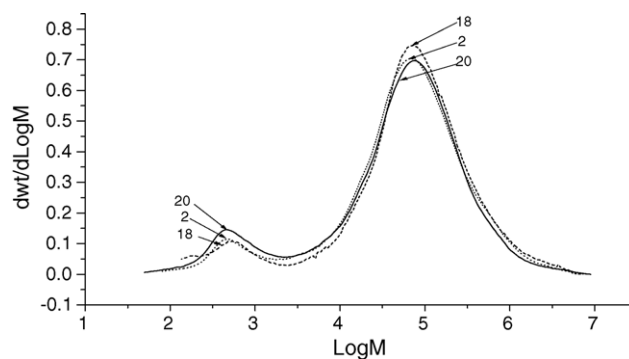


Fig. 9. GPC curves of PE prepared with **1** and different alkylaluminums: (2) AlEt₃, (18) Al(*i*-Bu)₃ and (20) AlHe₃ (numbers of the curves correspond to entries in Table 4).

of alkylaluminums could restrain β-H transfer of the catalytic species (a), which led to the *M*_{pk2} increasing.

3.3. AlHe₃ as activator

3.3.1. Effect of the temperature and Al/Fe ratio

To further confirm the above activation and polymerization mechanism, it was investigated that the catalyst system **1**/AlHe₃ polymerized ethylene under different conditions as seen in Table 5. With various polymerization temperature and Al/Fe ratios, the changes of the activity, *M*_{pk1} and *M*_{pk2} in the catalyst system **1**/AlHe₃ were very similar to those in the catalyst system **1**/AlEt₃. It was very clear that the low molecular weight materials had greater percentage and the *M*_{pk1} was the highest at the lower polymerization temperature such as the entries 21 and 22. With the polymerization temperature rising, the *M*_{pk2} decreased gradually. The activity was the highest and the *M*_{pk1} was the lowest at 25 °C. Possibly the low or high polymerization temperature benefited ethylene polymerization of the catalytic species (b), which produced higher *M*_{pk1} and greater percentage of the low molecular weight materials. The activity of the catalyst system was inversely correlative to the *M*_{pk1} and percentage of the low molecular weight materials. So the activity of the catalytic species (b) was lower than that of the catalytic species (a) generally. The higher Al/Fe ratio resulted in not only the decreasing of the activity but also increasing of the low molecular weight materials (in Fig. 10). In the entry 27, some of the low

Table 4
Ethylene polymerization catalyzed by complex **1** with different alkylaluminums and

| Entry | Alkylaluminum | Activity ^a | <i>M</i> _{pk} × 10 ^{-3b} (g/mol) | | <i>M</i> _w × 10 ^{-5b} (g/mol) | MWD ^b | <i>T</i> _m ^c (°C) |
|----------------|--------------------------------|-----------------------|--|--------|---|------------------|---|
| | | | Peak 1 | Peak 2 | | | |
| 2 ^d | AlEt ₃ | 13.7 | 0.474 | 70.1 | 1.78 | 39.7 | 133.0 |
| 18 | Al(<i>i</i> -Bu) ₃ | 13.0 | 0.555 | 72.9 | 1.96 | 44.7 | 134.5 |
| 19 | AlEt ₂ Cl | – | – | – | – | – | – |
| 20 | AlHe ₃ | 15.7 | 0.467 | 77.2 | 1.66 | 53.9 | 132.9 |

General polymerization conditions: [Fe] = 1.0 × 10⁻⁵ M, *P* = 1.0 bar, *t* = 30 min, *T* = 25 °C, Al/Fe = 200, solvent: hexane.

^a In 10⁶ g PE/mol Fe h.

^b Determined by means of GPC.

^c Measured by means of DSC.

^d [Fe] = 1.07 × 10⁻⁵ M

Table 5

Ethylene polymerization catalyzed by complex **1** with AlHe₃

| Entry | Temperature (°C) | Al/Fe (mol/mol) | Activity ^a | $M_{pk} \times 10^{-3b}$ (g/mol) | | $M_w \times 10^{-5b}$ (g/mol) | MWD ^b | T_m^c (°C) |
|-----------------|------------------|-----------------|-----------------------|----------------------------------|--------|-------------------------------|------------------|--------------|
| | | | | Peak 1 | Peak 2 | | | |
| 21 | -5 | 200 | 1.24 | 4.77 | 194 | 1.23 | 52.6 | 132.9 |
| 22 | 5 | 200 | 6.84 | 1.77 | 159 | 2.11 | 110 | – |
| 20 | 25 | 200 | 15.7 | 0.467 | 77.2 | 1.66 | 53.9 | 132.9 |
| 23 | 35 | 200 | 8.48 | 0.555 | 62.7 | 1.59 | 70.7 | – |
| 24 | 45 | 200 | 0.446 | 0.603 | 42.1 | 0.441 | 101 | 126.7 |
| 25 | 55 | 200 | Very low | – | – | – | – | – |
| 26 | 25 | 1000 | 18.1 | 0.403 | 80.0 | 1.09 | 103 | 129.9 |
| 27 | 25 | 2000 | 3.95 | 0.268 | 86.2 | 0.595 | 219 | 129.4 |
| 28 ^d | 25 | 2000 | 3.02 | 0.503 | 86.2 | 0.892 | 167 | 129.4 |
| 29 ^e | 25 | 2000 | 0.924 | 0.240 | – | 0.00200 | 1.54 | 45.9 |

General polymerization conditions: [Fe] = 1.0×10^{-5} M, $P = 1.0$ bar, $t = 30$ min, solvent: hexane.^a In 10^6 g PE/(molFe h).^b Determined by means of GPC.^c Measured by means of DSC.^d Insoluble fraction of the entry 27 in the solvent hexane at room temperature.^e Soluble fraction of the entry 27 in the solvent hexane at room temperature.

molecular weight materials were soluble in the solvent hexane at room temperature.

3.3.2. Structure characteristics of PE prepared with catalytic system **1**/AlHe₃

Similar to the catalytic system **1**/AlEt₃, the variations in the polymerization temperature and the amount of the AlHe₃ could affect the structures of PE prepared by catalytic system **1**/AlHe₃. The much more branched PE was prepared at high temperature or Al/Fe molar ratio compared to that at low temperature or Al/Fe molar ratio under the same conditions (in Fig. 11). The ¹³C NMR analyses of PE were measured as shown in Fig. 12. Besides isolated methylene carbons at 30.0 ppm, the entry 20 had least saturated end group carbons at 14.0 ppm, 22.8 ppm, 32.2 ppm and other carbons with different chemical shifts. As could be seen, PE from the entry 20 contained fewer branches and the fraction of the low molecular weight than the entries 28 and 29. The entry 29, which was the soluble fraction of the entry 27 in the hexane at room temperature, was completely

low molecular weight materials. There was most branched PE in the entry 29. So the bimodal PE prepared with catalytic system **1**/AlHe₃ was made up of linear polyethylene chains and a few branched polyethylene chains. And branched polyethylene chains mainly concentrated on the low molecular weight.

Moreover, vinyl end groups (114.5 ppm) and α -carbon (34.2 ppm) of the entry 29 appeared obviously [18]. It is well known that β -H elimination of progressing chains leads to vinyl end groups. And chain transfer to aluminum leads to saturated chain ends (14.0 ppm) [3,5]. So the PE of the entry 29 was produced by the way of the β -H elimination of progressing chains rather than by the way of the chain transfer to aluminum. So the fraction of the low molecular weight with highly branched polyethylene chains and vinyl end groups resulted from the catalytic species (b) by β -H elimination of progressing chains at high Al/Fe ratio. On the contrary, the fraction of the high molecular weight with linear polyethylene chains and saturated chain ends resulted from the catalytic species (a) by progressing chain transferring to alkylaluminum.

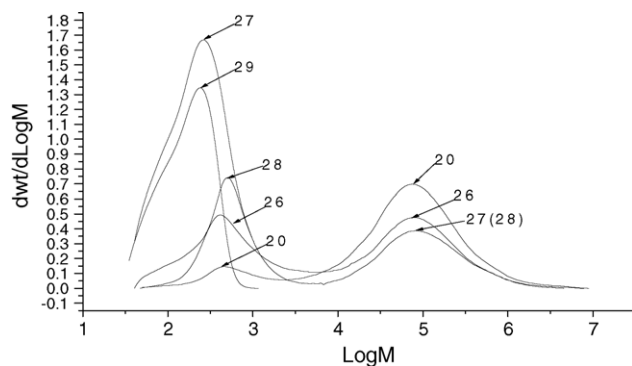


Fig. 10. GPC curves of PE prepared with catalytic system **1**/AlHe₃ at various Al/Fe molar ratios: (20) Al/Fe = 200, (26) Al/Fe = 1000, (27) Al/Fe = 2000, (28) Al/Fe = 2000 and (29) Al/Fe = 2000 (numbers of the curves correspond to entries in Table 5).

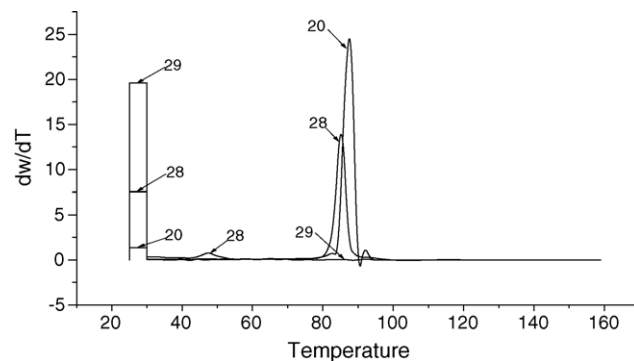


Fig. 11. CRYSTAF curves of PE prepared with catalytic system **1**/Al(*m*-He)₃ at various Al/Fe ratios: (20) Al/Fe = 200, (28) Al/Fe = 2000 and (29) Al/Fe = 2000 (numbers of the curves correspond to entries in Table 5).

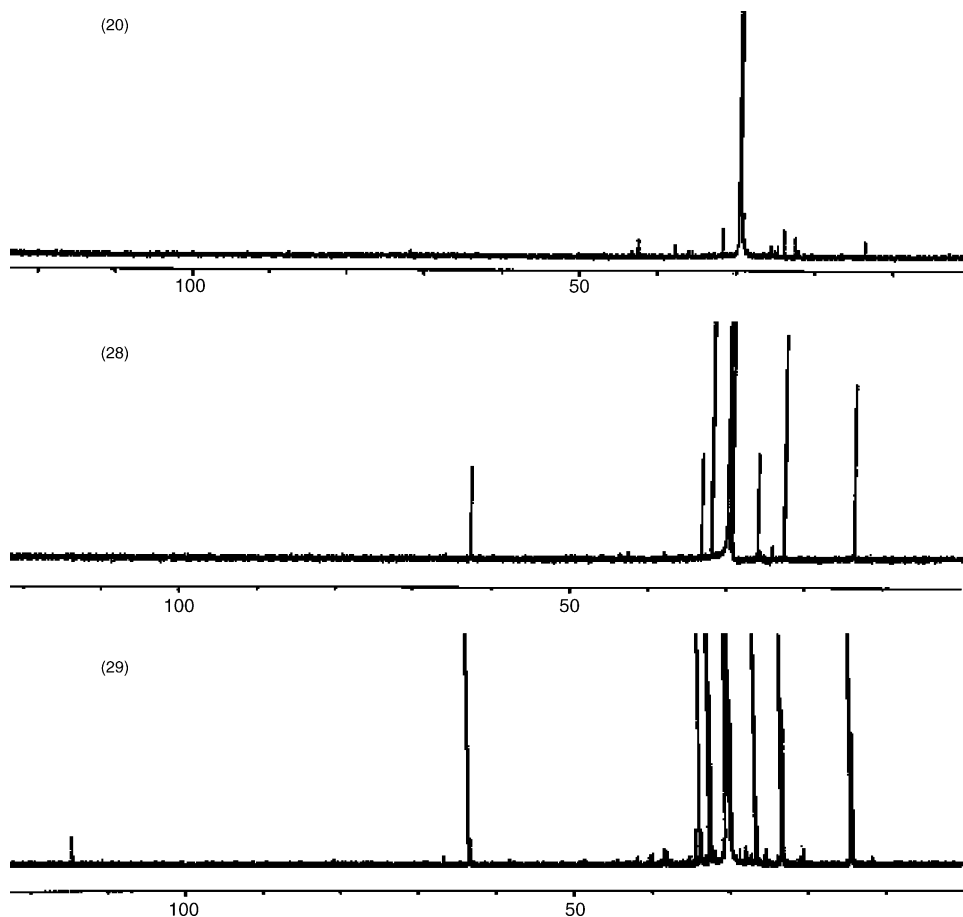
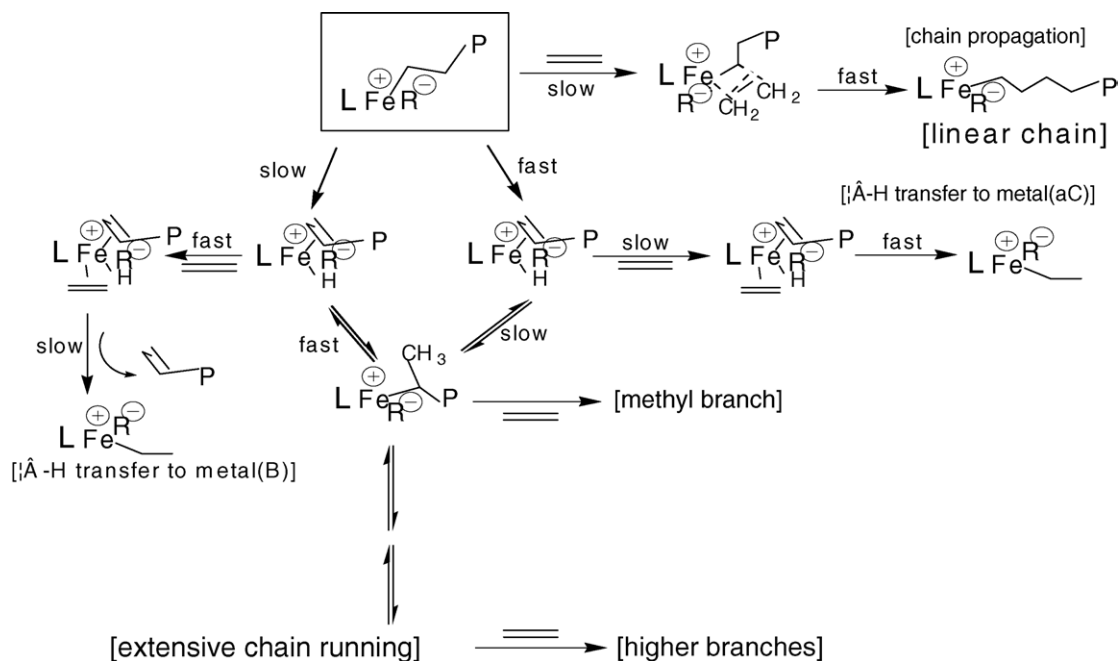


Fig. 12. ^{13}C NMR curves of PE prepared with catalytic system $1/\text{Al}(n\text{-He})_3$: (20) $T = 25^\circ\text{C}$, $\text{Al}/\text{Fe} = 200$; (28) $T = 25^\circ\text{C}$, $\text{Al}/\text{Fe} = 2000$; (29) $T = 25^\circ\text{C}$, $\text{Al}/\text{Fe} = 2000$ (numbers of the curves correspond to entries in Table 5).



Scheme 2. Branched mechanism of ethylene polymerization with the catalytic system $1/\text{AlR}_3$.

3.4. Activation, polymerization and branched mechanism of ethylene polymerization with the catalytic system $1/AlR_3$

On the basis of the above results and discussions, it was completely possible that two different kinds of catalytic species whose ratios varied with changing Al/Fe ratio existed in the catalytic system $1/AlR_3$. When Al/Fe molar ratio was below 1000 and polymerization temperature was moderate, the catalytic species (a) possibly predominated in the catalytic system. The catalytic species (a) with very high activity mainly produced linear PE with high molecular weight in the bimodal PE prepared with the catalytic system. However, the catalytic species (b) was primary at high Al/Fe molar ratio above 2000 or high polymerization temperature. The catalytic species (b) with low activity mainly produced branched PE of low molecular weight in the bimodal PE prepared with the catalytic system. The activity of the catalytic species (b) was higher than that of the catalytic species (a) at very low polymerization temperature. So low molecular weight materials had more percentage and higher M_{pk1} at very low polymerization temperature. The difference between two catalytic species was the electronic property and steric bulk of the anions. The catalytic species (a) was a loose ion pair that benefited the insertion of ethylene monomers. At the same time, withdrawing electrons of Cl anion strengthened the electrophilic properties of the Fe cation. So the catalytic species (a) had very high activity. However, the catalytic species (b) was a compact ion pair that held back the insertion of ethylene monomer. Relatively providing electrons of R anion weakened the electrophilic properties of the Fe cation. So the activity of the catalytic species (b) was very low. Meanwhile, the two kinds of catalytic species had similar chain propagation, chain transfer and chain termination behavior in ethylene polymerization.

In addition, branched mechanism of the catalytic species (b) was similar to that of α -diimine Ni catalysts as shown in Scheme 2. Because of its low activity, the catalytic species (b) had enough time to undergo a series of β -hydride eliminations and re-additions, which resulted in the metal migrating or walking. Then trapping of these species followed by ethylene insertion resulted in the formation of a branch in the growing polymer chain backbone. The catalytic species (b) mainly produced branched PE with low molecular weight.

4. Conclusion

The ethylene polymerization characters of the catalytic systems $1/AlR_3$ had been described. These catalytic systems produced bimodal polymers with a little short branch depending on the polymerization conditions. The bimodal behavior was possibly ascribed to two catalytic species in the catalytic systems. Two different kinds of catalytic species whose ratios varied with

changing Al/Fe ratio had been identified: the catalytic species (a) that mainly produced linear PE with high molecular weight in the bimodal PE and the catalytic species (b) that mainly produced branched PE with low molecular weight in the bimodal PE. Each of them had different natures for ethylene polymerization, respectively, allowing the resultant M_{pk1} , M_{pk2} , M_w and MWD of the prepared PE to be systematically altered. Work is in progress to make the nature of the active site in the catalytic systems clearer, in particular, the role and influence of anion, which would allow further rational modification of these catalytic systems.

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