Characterization of Compositional Heterogeneity in the Polyethylene Prepared with Bis(imino)pyridyl Iron(II) Precatalyst and Triethylaluminum

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ABSTRACT: Analytical tools including solvent gradient elution fractionation (SGEF), GPC, ^{13}C NMR, and differential scanning calorimetry (DSC) are integrated for the characterization of compositional heterogeneity in the polyethylene (PE) prepared with the $LFeCl_2/AlEt_3$ catalytic system. The results indicate that at least two different kinds of catalytic species are present in ethylene polymerization. One active species generating branched PE gives low molecular weight; another kind of active species gives high molecular weight PE with high linear structure. The amount of branch decreases with increasing the molecular weights, and the small proportion of the branched PE shows low molecular weight with vinyl-terminated end group, indicating that the branched PE is generated from the catalytic species giving low activity. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1151–1155, 2009

Key words: polyethylene; iron catalysts; solvent gradient elution fractionation; DSC; ^{13}C NMR

INTRODUCTION

Brookhart's diimine nickel catalysts[1] and Grubbs' activator-free iminophenolate nickel catalysts[2] produce branched polyethylenes. However, the bis(imine)pyridine iron and cobalt, discovered by Brookhart[3] and Gibson,[4] produce highly linear high density polyethylene (PE) and require α-olefin introduction to create short branch chain. Recently, it was reported that common alkylaluminum compounds, such as triethylaluminum ($AlEt_3$) and triisobutylaluminum (Al (i-Bu)$_3$), were also the effective activators in ethylene polymerization with iron and nickel-based complexes.[5–7] Furthermore, the alkylaluminum compounds or aluminoxanes acted as chain-transfer agents and therefore affected the molecular weights and molecular weight distributions (MWDs) of the polymers.[8,9] In our previous work,[10] we reported that the polymerization temperature and the molar ratio of Al/Fe had a remarkable effect on the catalytic activities, molecular weights, MWDs, and PE microstructures in the ethylene polymerization with the complex $LFeCl_2$ (L = 2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine) activated by AlR_3 (R = Et, ^{t}Bu, or He).

To get further insights about the relationship between the microstructure of PE and polymerization mechanism, the investigation of PE structural heterogeneity is carried out using SGEF, ^{13}C NMR, and DSC analytical techniques. Solvent gradient elution fractionation (SGEF), a technique used to fractionate semicrystalline polymers according to their solubility-Mw relationship, has been widely used for the characterization of the compositional heterogeneity of polyolefins.[11–13] It is widely accepted that ^{13}C NMR is a powerful tools to study the comonomer incorporation and polyolefin copolymers sequence distribution.[14–16]

In this work, the composition and distribution of PE sample prepared with the catalyst system $LFeCl_2/AlEt_3$ were investigated using the analytical tools such as SGEF, GPC, ^{13}C NMR, and DSC. Through the detailed analysis, it was found that PE made in this system is composed of both the linear part and branched part. Additionally, it is proposed that the formation of low molecular weight part of PE was ascribed to both β–H elimination termination of the progressing chain and the chain transfer to alkylaluminum, which further supports the previously proposed mechanism for bimodal PE formation, that is, two different kinds of catalytic species presenting in this catalytic system $LFeCl_2/AlEt_3$.[10]

EXPERIMENTAL

Materials

The PE sample was prepared according to the published procedures.[10] 1,2,4-Trimethylbenzene (TMB,

TABLE I
The Analysis Results of Polyethylene Prepared with Bis(imino)pyridyl Iron(II) Precatalyst and AlEt₃

Fraction	Percent (%)[a]	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	MWD	T_m (°C)	T_c (°C)	Crystal X_c (%)[b]	Branch[c]	Unsaturated ends[c]	Saturated ends[c]
Samp	100	3.88	12.7	32.6	133.0	114.3	71.97	Trace	–	–
1	2.43	0.72	0.083	1.1	86.5	79.3	54.00	1.5	0.7	34.2
2	6.41	2.10	0.41	1.9	125.4	111.1	64.19	0.43	1.6	10.5
3	3.10	9.61	1.10	1.2	131.5	117.5	70.26	0.40	1.0	2.0
4	27.31	22.9	2.97	1.3	134.7	118.5	78.22	0.38	0.4	0.7
5	56.43	90.1	23.1	2.6	137.5	114.6	66.35	0.34	Trace[d]	0.3
6	4.04	90.7	25.6	2.8	137.7	115.5	63.77	0.29	Trace[d]	0.2
7	0.20	ND[e]	ND	ND	ND	ND	ND	ND	ND	ND

[a] Initial sample weight is 9.3152 g, and the sum of fractions is 9.0839 g (recovery, 97.52%).
[b] Obtained by the DSC, $X_c\% = \Delta H_m / \Delta H^{\theta}_m \cdot 100\%$, $\Delta H^{\theta}_m = 285.5$ J/g.
[c] Results from ^{13}C NMR analysis, given per 1000 carbon atoms.
[d] ≪0.1/1000.
[e] Not determined.

≥98%) and ethyleneglycol-monobutyl-ether (BCS, ≥99%) were bought from J. T. Baker Chemicals and Tianjin Chemical Reagent Corp., respectively, and used without further purification. 2,6-Di-*tert*-butyl-4-methyl-phenol (BHT, ≥99%) was obtained from Jinke Institute of Fine Chemical Industry and used as received.

Fractionation of polymers

For fractionation according to molecular weight, SGEF was carried out at 135°C using TMB (solvent) and BCS (nonsolvent). The preparative SGEF equipment used in this work was similar to the typical preparative temperature rising elution fractionation equipment. The sample (9.3152 g) was dissolved in 700 mL of TMB at 140°C. BHT (3.0 g/L) was added to the extracting solvent as antioxidant reagent. The polymer solution was introduced to the column at 140°C packed with 60–80-mesh glass beads. Then the column was slowly cooled down to 25°C according to the programmed procedure (from 140°C to 100°C in 8 h, from 100°C to 90°C in 48 h, from 90°C to 80°C in 96 h, from 80°C to 70°C in 48 h, from 70°C to 40°C in 60 h, from 40°C to 25°C in 30 h, held at 25°C for 24 h). The fraction **1** was obtained, which is the dissolvable PE at 25°C. The fractionation procedure was performed at 135°C by increasing TMB/BCS volume ratio. Extraction took place over the range of TMB/BCS volume ratio from 0/100 to 100/0 divided into six steps (fraction **2**: 0/100, fraction **3**: 10/90, fraction **4**: 34/66, fraction **5**: 55/45, fraction **6**: 66/34, and fraction **7**: 100/0). During each step, the column was allowed to equilibrate at the set mixed solvent for 16 h before it was eluted with 1200 mL of the mixed solvent (800 mL/h). Each fraction was obtained by elution of two times (1200 mL/time). Three-hour interval is needed for the dissolution equilibration before the next elution. The eluted solution of two times was cooled, precipitated with

twice of the volume of acetone, and filtered. The obtained polymer fractions were then dried in a vacuum oven at room temperature until constant weight.

Characterization of polymers

Molecular weight and 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.

Differential scanning calorimeter (DSC) was carried out with a PerkinElmer DSC-7. The sample was heated from 0 to 160°C at a rate of 10°C/min and cooled down at the same rate to 0°C. The second heating cycle at 10°C/min was used for data analysis. ^{13}C NMR spectra of PE was 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: 10 mm probe; acquisition time, 5 s; relaxation time, 10 s; numbers of scans, 5000.

RESULTS AND DISCUSSION

The results of the original sample and the fractionations

Some previous data concerning the original sample and its fractions are summarized in Table I. The total recovery of SGEF fractionation was 97.52% and seven fractions were obtained. The MWD of every fraction is about 2.0. The results demonstrated that the PE sample was eluted over a wide range of TMB/BCS volume ratio, indicating the heterogeneity in both molecular weight and chain microstructure.

The GPC curves of SGEF fractions and the original sample are shown in Figure 1. The molecular weights of the fractions increase with TMB/BCS volume ratio increasing. The increase of the molecular
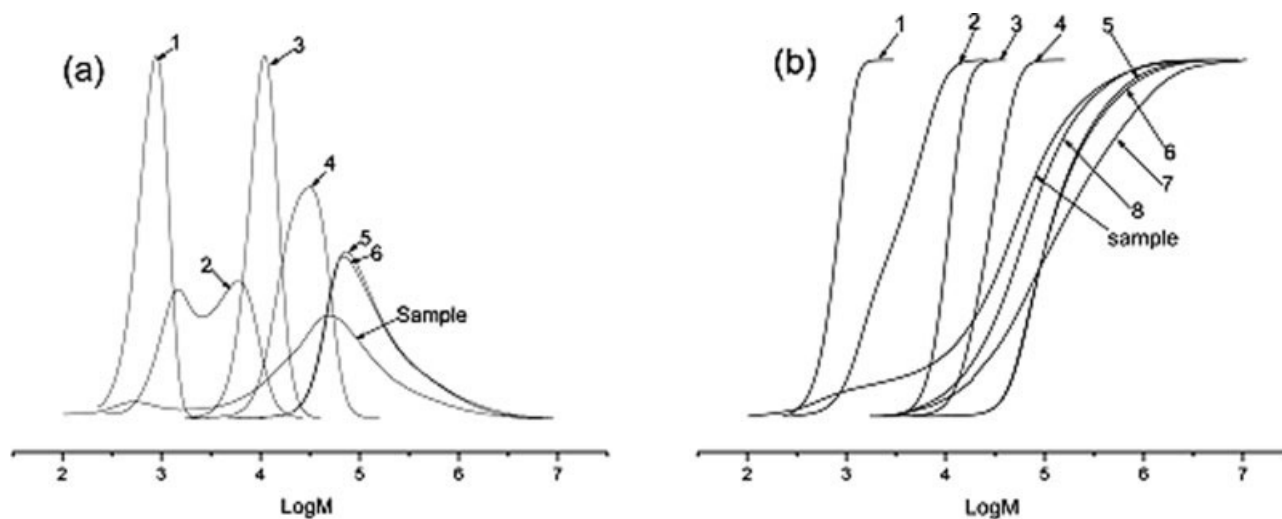
Figure 1 GPC curves of the PE sample and every fraction. (a) Differential curves and (b) Integral curves. (Numbers of the curves correspond to fractions in Table I.)

weight of the fractions with TMB/BCS volume ratio might be due to the coincidence between molecular weight and chain regularity.[17] The fraction **1** is part of the original sample with low molecular weight. The fraction **2** shown bimodal in GPC curve is a transitional fraction between the low molecular weight part and the high molecular weight part. The fractions **3–7** consist of the high molecular weight part of the original sample. The molecular weight and MWD of the fraction **6** are similar to that in fraction **5**. The problem is possibly from the dissolution equilibration due to the large percentage of fraction **5**. However, the quantity of the fraction **7** is too less to be precisely characterized.

Characterization of SGEF fractions using ^{13}C NMR and DSC

A typical result of SGEF is given in Table I. It was found that fractions with considerably narrow MWD were obtained by this technique. The properties of molecular chain are influenced not only by the molecular weight, but also by the structure of molecular chain.

To further investigate PE structures, ^{13}C NMR was used to analyze the molecular chain structure. As shown in Table I, the fractions have different end group structures and different degrees of short chain branch (SCB), which can also be seen from Figure 2. Besides the isolated methylene carbons at 30.0 ppm, vinyl end groups (114.2 ppm) and α-carbon (33.9 ppm) are also appeared obviously in the fraction **1**.[18] And the chain ratio of unsaturated end group to the saturated end group increases from 0.7/16.7 to 0.4/0.15 with the molecular weight increasing in the fractions **1–4**. The fractions **5** and **6** with high molecular

weight had few unsaturated end group. Moreover, the fraction **1** contains methyl branches (21.8 ppm, 22.5 ppm) with the degree of SCB 1.5/1000C.[19,20] As the molecular weights of the fractions increase, the degree of SCB decreases significantly as shown in Figure 3. The nomenclature used to designate the different carbon types is introduced by Usami and Takayama.[21] Branches are named by xBn, where n is the length of the branch and x is the carbon number starting with the methyl group as "1." For the backbone carbons, Greek letters and "br" are used instead of x for the methylenes and a branch point, respectively. The shift at 21.8 ppm is $1B_1(PPE)$ and 22.5 ppm is ascribed to $1B_1(PPP/mm)$. The shifts at 29.0, 33.4, 38.1, and 46.6 ppm are assigned to $brB_1(PPP/mm)$, $brB_1(PPE)$, $\alpha\gamma(PPE)$, and $\alpha\alpha(PPP/mm)$ carbons.[19,20] Signals at 24.4, 26.2, and 63.0 ppm have no exact assignment, which might result from the degradation of the PE.

In the ethylene polymerization using Bis(imino)-pyridyl iron(II) catalysts, the vinyl-terminated end group is due to the β–H elimination, while the saturated end group results from the chain transfer to alkylaluminum.[3,8] Consequently, the fractions of high molecular weight with little unsaturated end group were mainly formed by the chain transfer to alkylaluminum in the ethylene polymerization using $LFeCl_2/AlEt_3$ catalyst system. And the other fractions of low molecular weight were produced by both β–H elimination and the chain transfer to alkylaluminum. The ratio of two kinds of chain termination (β–H elimination/chain transfer to alkylaluminum) increases from 0.7/16.7 to 0.4/0.15 with the molecular weight increasing in the fraction **1–4**. Additionally, no molecular chains with complete saturated end group, but some molecular chains with
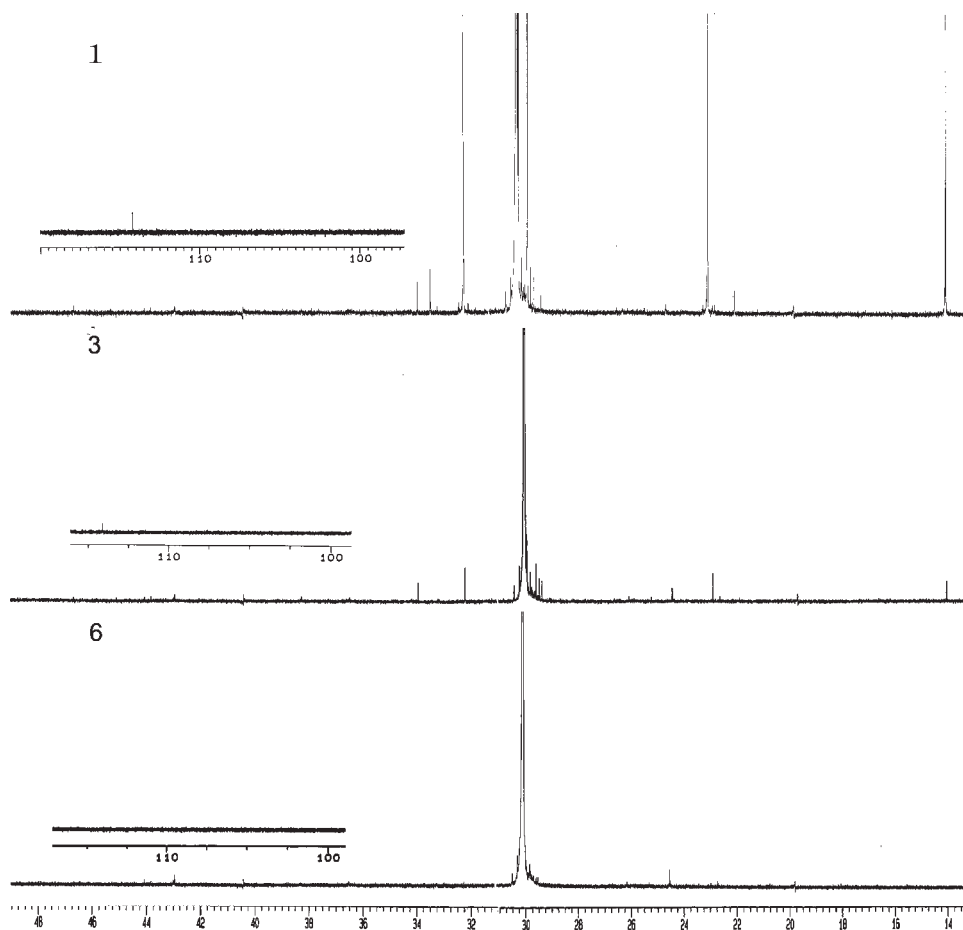
Figure 2 ^{13}C solution NMR spectra of SGEF fractions. (Numbers of the curves correspond to fractions in Table I.)

unsaturated end group in the fraction **1** indicates that a small proportion of the fraction **1** with the lowest molecular weight is due to the β–H elimination. It is obvious that not only the low molecular weight part (the fraction **1** and the fraction **2**) but also the high molecular weight part (fractions **3–7**) result from two kinds of chain termination. Therefore, it is well reasonable to propose that two kinds of catalytic species are present in the catalytic system, which can be used as an alternative explanation for the bimodal behavior. Each catalytic species having relatively independent chain propagation, chain transfer, and chain termination produces each part of bimodal PE.

In addition, the DSC measurements results of every fraction are consistent with the results of GPC and ^{13}C NMR as shown in Table I. Because of the crystalliability coincidence between molecular weight and chain regularity, the melting points (T_m) increase with the molecular weights increasing.

Based on the above results and discussions, two kinds of molecular chain structures in PE samples indicate that two kinds of catalytic species (a) and (b) possibly exist in the LFeCl$_2$/AlEt$_3$ catalytic system as shown in Scheme 1.[10,21,22] The catalytic species (a) giv-

ing very high catalytic activity produces mainly linear PE with high molecular weight in the bimodal PE sample according to the proposed polymerization mechanism.[8] The catalytic species (b) exhibiting low catalytic activity produces mainly branched PE with low molecular weight. Meanwhile, these two kinds of catalytic species have similar chain propagation, chain transfer, and chain termination behavior in ethylene
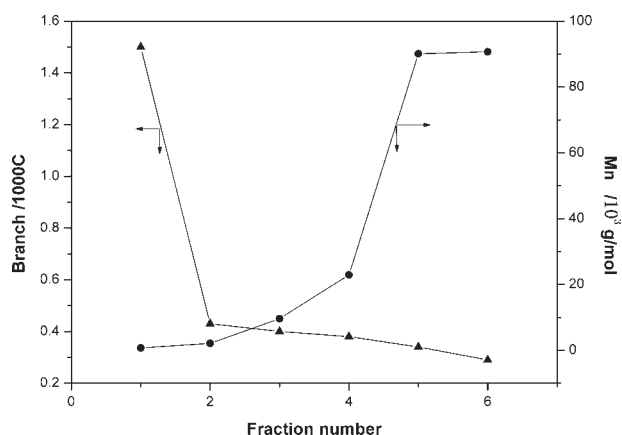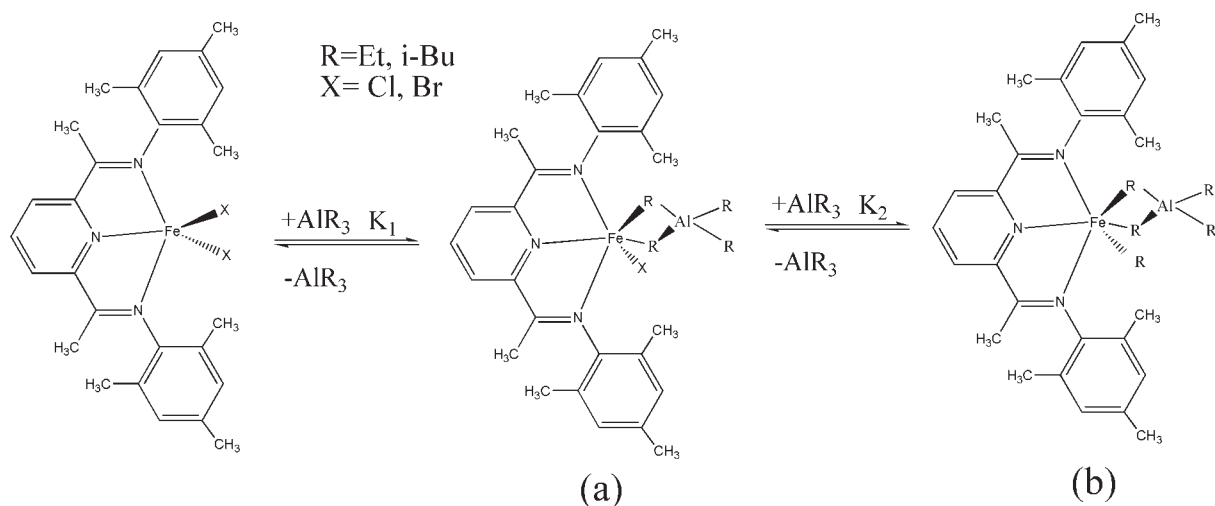

Figure 3 Molecular weight and branches of SGEF fractions.

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

polymerization. The mechanism for producing branched PE with the catalytic species (b) might be similar to that in α-diimine Ni catalysts.[10,23,24] Because catalytic species (b) had low activity, it had enough time for β-hydride eliminations and reinsertion, which could be described as the chain migrating or walking. As a consequence, the low molecular weight oligomer/polymer with vinyl-terminated end group can be incorporated in ethylene polymerization, which can generate the branching.

CONCLUSIONS

The combination of SGEF, GPC, ^{13}C NMR, and DSC can provide more detailed information concerning the polymer composition and microstructure. In the case PE homopolymer made with the $LFeCl_2/AlEt_3$ catalytic system, at least two different kinds of catalytic species are present in ethylene polymerization, which make the perfect bimodal PE. The PE should be considered an *in situ* polymer blend of the branched PE with low molecular weight and the linear PE with high molecular weight.

The SCB of fractions decreases with increasing molecular weights, and the small proportion of the PE are branched PE with low molecular weight and unsaturated end group, indicating that the branched PE results from the catalytic species having low activity.

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