

Reactor Blending of Polyethylene with Ethyl-Bridged Zirconocene Catalyst and Iron-Based Diimine Complex

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ABSTRACT: Blends of polyethylene (PE) were produced in a single reactor using a combination of $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ [Ar=2,6-2CH₃(C₆H₄)] and *rac*-Et(Ind)₂ZrCl₂. The experimental results showed that the PEs obtained have a broad molecular weight distribution (MWD) and both the molecular weight and the MWD can be regulated through changing the mole ratio of the two active sites. In addition, the polymerization activities decreased with the increase of the Fe/Zr mole ratio whereas the crystallinity of the PE obtained exhibited a contrary trend, decreasing as the Fe/Zr mole ratio went up. The morphology of the blends also directly relates to the Fe/Zr mole ratio, and more iron content in the bimetallic catalysts system

gives rise to compact PEs of high crystallinity. This reflects that the reactor blends are morphology controllable as well and can be easily applied to present processing techniques because of adjustable molecular weights and their distribution. Differential scanning calorimetry, thermogravimetric analysis, gel permeation chromatography, and scanning electron microscopy were employed to characterize the properties of the reactor blends of PEs. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1515–1518, 2003

Key words: blending; polyethylene; metallocene catalysts; transition metal chemistry

INTRODUCTION

In polymer processing the weight-average molecular weight (M_w) and molecular weight distribution (MWD) basically determine the mechanical and rheological properties of polymers. An increase in the MWD for polyethylene (PE) is beneficial for blowing and extrusion techniques.¹ Thus, it is necessary to control the M_w and MWD of polymers to attain excellent properties.

There are three present methods for controlling the M_w and MWD of polymers. The first is physical blending of polymers with different M_w values. Although it is effective to control the M_w and MWD of polymers, dealing with the accompanying miscibility problems is difficult. The second method involves using a series of reactors in which polymerization proceeds under different conditions. It is also impractical for commercial processes and increases capital cost. The third is to combine two or more catalysts in a single reactor and produce polymers with different M_w values.

The emphasis of the last method has focused thus far on a Ziegler–Natta/metallocene hybrid catalyst,² early/late transition metal catalyst combinations,³ and a metallocene/metallocene hybrid catalyst.⁴ The coordination chemistry of heterobimetallic complexes combining early and late transitions has been of considerable interest,⁵ and such complexes have also been applied to polymerization of olefins.^{6,7} However, to the best of our knowledge, evidence has yet to be reported for iron complexes with related tridentate nitrogen ligands in combination with ethyl-bridged zirconocene to carry out ethylene polymerization.

This is the first article to report on the simultaneous polymerization of ethylene by a combination of $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ [Ar=2,6-2CH₃(C₆H₄)] and *rac*-Et(Ind)₂ZrCl₂. Blends of PEs are obtained in a single reactor.

EXPERIMENTAL

Materials

The catalyst 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron chloride (**1**) was synthesized following the method described in the literature.⁸ The *rac*-Et(Ind)₂ZrCl₂ catalyst (**2**) was purchased from Aldrich Corp. (Milwaukee, WI). Polymerization grade ethylene was obtained from Yanshan Petro-Chemical Ltd. and used without further purification. A methyl aluminoxane (MAO) solution in toluene (1.4 mol/L) was purchased from Albemarle Corp. Toluene and

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TABLE I
Data of Ethylene Polymerization Using Bimetallic Catalysts 1 and 2

Entry	Fe (μmol)	Zr (μmol)	Fe/Zr (mol/mol)	Activity $\times 10^{-6}$ ^a [g/(mol h)]	T_m ($^{\circ}\text{C}$)	X_c (%)	T_{onset} ($^{\circ}\text{C}$)	$M_w \times 10^{-4}$ (g/mol)	MWD
1	2.0	0	—	5.91	131.5	85.9	458.6	5.53	3.16
2	2.0	0.5	4	4.74	129.5	84.9	455.0	5.08	5.16
3	1.5	0.5	3	4.46	129.3	84.7	451.4	4.02	11.2
4	2.0	1.0	2	4.14	130.0	81.3	446.9	4.33	12.0
5	1.0	1.0	1	4.12	130.3	80.5	433.1	4.73	12.2
6	1.0	2.0	1/2	3.21	129.6	78.3	456.9	5.29	13.9
7	0.5	1.5	1/3	2.95	129.4	76.6	456.7	6.77	17.3
8	0.5	2.0	1/4	2.76	127.8	68.2	449.6	7.95	13.1
9	0	2.0	0	2.52	132.1	53.0	441.2	9.58	2.6

Polymerization conditions: 100 mL toluene, 50 $^{\circ}\text{C}$, 30 min, Al/(Zr + Fe) = 1500.

^a The activity is calculated with the sum of Fe plus Zr.

tetrahydrofuran were refluxed with sodium and benzophenone and freshly distilled before use. All other chemicals were obtained commercially and used as received.

Characterization

The melting temperatures (T_m) of PE were determined by differential scanning calorimetry (DSC) with a DSC-7 (Perkin–Elmer) operating under nitrogen at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 20 to 150 $^{\circ}\text{C}$, and the T_m was determined from the second scan. The temperatures of maximum weight loss (T_{onset}) were measured by thermogravimetric analysis (TGA) on a TGA 7 series system apparatus (Perkin–Elmer). The M_w and MWD of PE were investigated with gel permeation chromatography (GPC) on a high-temperature GPC instrument (150CV Plus, Waters). Scanning electron microscopy (SEM, Hitachi-530) was employed to observe the morphology of the PE blends we obtained.

Ethylene polymerization

To a 250-mL thermostated flask were added 100 mL of toluene and MAO in a predetermined amount. The mixture was stirred for 5 min before the desired amount of catalysts 1 and 2 were transferred simultaneously and ethylene was introduced at atmospheric pressure. After 30 min the reaction was quenched with ethanolic hydrochloric acid. The polymer was kept in an excess of 10 vol % ethanolic solution overnight and then washed with ethanol and water in a Büchner funnel, separated, and dried in a vacuum at 70 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Ethylene polymerization was performed at atmospheric ethylene pressure in toluene and using MAO as the cocatalyst. Table I shows the results of the ethylene polymerization runs with different Fe/Zr molar ratios. The ethylene polymerization reaction

performed at 50 $^{\circ}\text{C}$ with 1/MAO showed higher activity than with 2/MAO as can be seen by comparing entry 1 (5.91×10^6 g of PE/mol[Fe] h) and entry 9 (2.52×10^6 g of PE/mol[Zr] h) in the table. This result agrees with the fact that late transition metal catalysts exhibit high ethylene polymerization activity at medium and low (sometimes even below 0 $^{\circ}\text{C}$) temperatures whereas zirconocene complexes generally exhibit better catalytic activities at higher temperatures.

Entries 2–8 in Table I show that varying the Fe/Zr molar ratio with a constant Al/(Fe+Zr) molar ratio influences the polymer properties and overall activity. Table I displays the dependence of the activity on the Fe/Zr molar ratio. The polymerization activity gradually drops as the Fe/Zr molar ratio is lowered and no maximum activity was found in this bimetallic catalyst system, which is different from ethylene polymerization using nickel and titanium complexes.⁹ This behavior might be attributed to the fact that the catalytic precursors work relatively independently, thus showing little synergic effect.

The TGA tracks, DSC traces, GPC profiles, as well as SEM images, were determined in order to obtain more

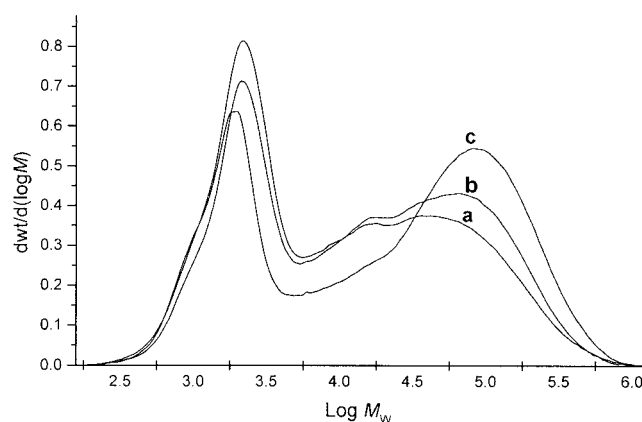


Figure 1 GPC traces of PE 1/2 = 3 (curve a), 1/2 = 1 (curve b), and 1/2 = 1/3 (curve c).

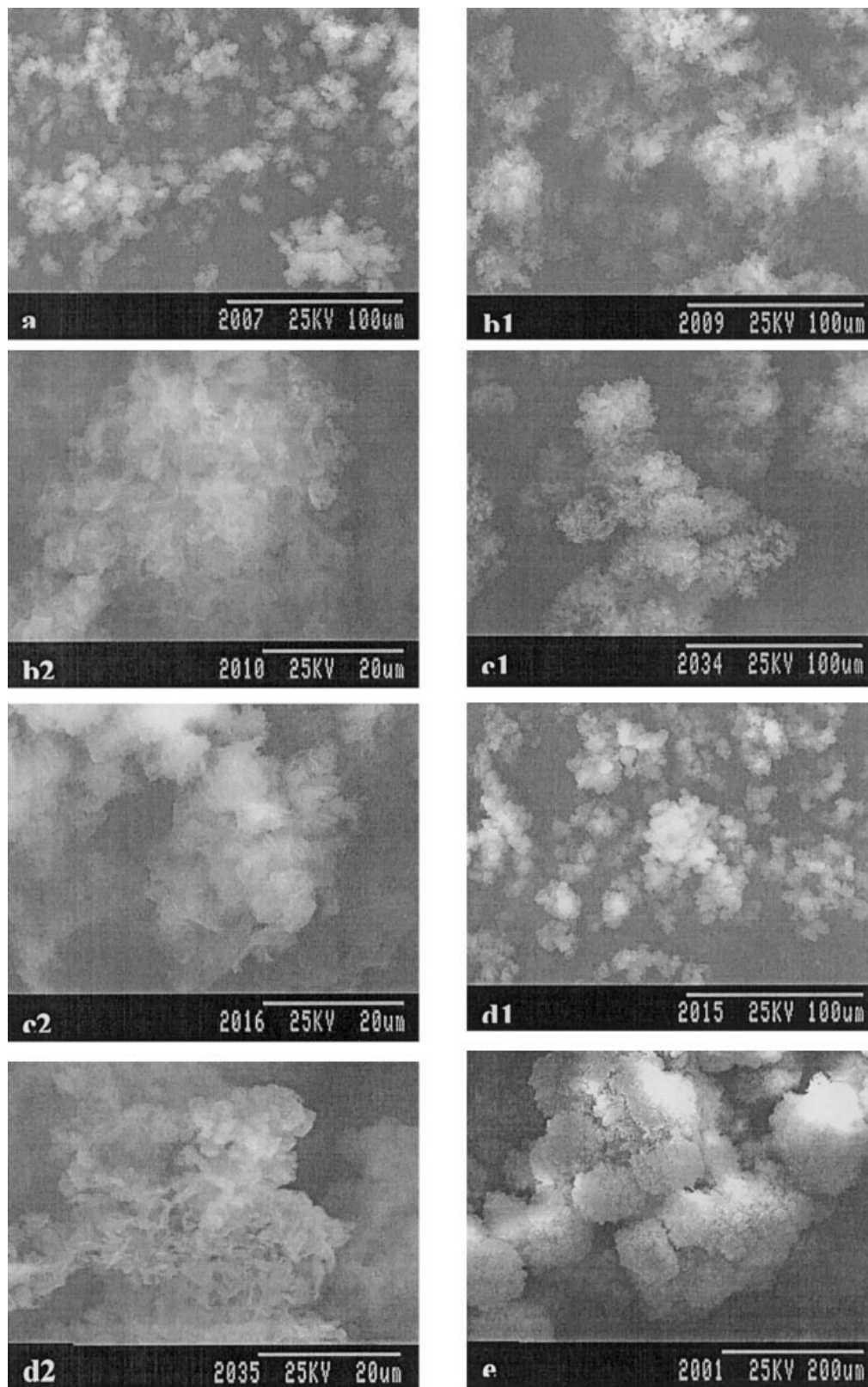


Figure 2 SEM images of PE from (a) 1, (b1,b2) $1/2 = 3$, (c1,c2) $1/2 = 1$, (d1,d2) $1/2 = 1/3$, and (e) 2.

details of the properties of PE blends and the dependence of these properties on the Fe/Zr molar ratio.

The TGA data in Table I show that the T_{onset} first decreases and then increases after experiencing a mini-

mum value of 433.1°C with a decrease in the Fe/Zr molar ratio employed in ethylene polymerization reactions. It shows that the PE blends possess adjustable T_{onset} values and are beneficial for physical processing.

The DSC data reflected that the degree of crystallinity (X_c) decreases with decreases in the Fe/Zr molar ratio from 85.9 to 53.0% whereas the T_m changes a little, except for the T_m values of PEs from **1**/MAO and **2**/MAO, which are higher than that of the reactor blends of PE. Now that the blends are formed under two catalysts, broad melting peaks are found in their DSC curves.

Correspondingly, the GPC profiles (Fig. 1) showed the same behavior as those determined by DSC measurements. It was observed that the MWD increases from 5.16 (Table I, entry 1) to the maximum value of 17.3 (Table I, entry 7; Fig. 1, curve c) when the Fe/Zr molar ratio is varied from 4 to 1/3, and it decreases as more Zr is used in the bimetallic catalyst system. It is well known that a late transition metal alone can polymerize ethylene to PE with a broad MWD and even a highly branched PE under certain conditions. However, producing a PE with an MWD as high as 17.3 and easily controllable morphology on a single catalyst is rarely reported and it is practical to combine a late transition metal complex and a metallocene catalyst in order to obtain a PE with the desired MWD. It is also seen from Figure 1 that the PE obtained is bimodal and each can be attributed to a kind of active site; the peaks represent high molecular weight corresponding to *rac*-Et(Ind)₂ZrCl₂ and those of low molecular weight mainly being from $\{[(2\text{-ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$ [Ar=2,6-2CH₃(C₆H₄)].

The results obtained from SEM measurements clearly show the morphology evolution as the Fe/Zr molar ratio changes in the reactor blending process. Figure 2 shows that catalyst **1** alone catalyzes ethylene to a PE of fine cotton-like particles [Fig. 2(a)], which have low molecular weight and are easy to crystallize, a point also embodied in the data of Table I. As the Fe/Zr molar ratio decreases PE blends are obtained, and their morphologies change from being like cotton wadding [Fig. 2(b1,b2)] to compact agglomerates with irregular particles [Fig. 2(d1,d2)] until a large spherical

PE from catalyst **2** alone is obtained [Fig. 2(d1,d2)]. In other words, the morphology of PE blends can be controlled via adjusting the Fe/Zr molar ratio.

CONCLUSIONS

PE blends can be obtained using a simultaneous combination of a late transition metal complex and a zirconocene catalyst with MAO as the cocatalyst in a single reactor. Properties such as the temperatures of melting, temperatures of maximum weight loss, and polymerization activity can also be controlled. In addition to their broad adjustable MWD, the morphology of the PE blends that we obtained can be easily regulated; hence, they have better processability.

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