Synthesis of Reactor Blend of Linear and Branched Polyethylene Using Metallocene/Ni-Diimine Binary Catalyst System in a Single Reactor

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ABSTRACT: This work reports the synthesis of a series of reactor blends of linear and branched polyethylene materials using a combination of [1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide] (**1**)/MMAO, known as an active catalyst for the production of branched polyethylene, and [rac-ethylenebis(indenyl) zirconium dichloride] (**2**)/MMAO, which is active for the production of linear polyethylene. The polymerization runs were performed at various levels of temperature, pressure, and catalyst **2** molar fractions. At 5°C, there was very low influence of catalyst **2** molar fraction on the overall catalyst activity. However, at 30°C and 50°C, the overall catalyst activity increased linearly with catalyst **2** molar fraction. The same linear dependency was also found for the polymerization reactions carried out at 60°C and 100°C. At various levels of temperature and ethylene pressure, higher melting temperature and crystallinity were observed with an increase in catalyst **2** molar fraction. At 60°C and 100 psig, the DSC thermograms of the polymers produced with **1**/**2**/MMAO exhibited two distinct peaks with melting temperatures closely corresponding to the melting temperatures of the polymers produced with the individual catalysts, **1**/MMAO and **2**/MMAO. The GPCV analysis of all polyethylene samples showed monomodal molecular weight distributions with low polydispersities. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2212–2217, 2005

Key words: polyethylene (PE); synthesis; branched; blends; metallocene catalysts

INTRODUCTION

Single site olefin polymerization catalysis has evolved considerably since the discovery of metallocene catalysts in the early 1980s. Metallocene catalysts have been well known for their excellent flexibility and versatility for the synthesis and control of polyolefin structure.[1] Compared to the conventional Ziegler Natta catalyst, these single type catalysts are highly active and can produce polymers with narrow molecular weight distribution and narrow chemical composition distribution.[1] In addition to metallocene catalysts, another milestone in the area of olefin polymerization catalysis was the discovery of the homogeneous single site α-diimine based late transition metal catalysts (Ni and Pd) in 1995.[2] Different from metallocenes, these catalysts can produce polyethylene with branch structure without the use of α-olefin comonomers.[2–9] Simple control over the catalyst structure and polymerization conditions (ethylene pressure and reaction temperature) allows one to readily produce a wide range of polyethylene grades from highly branched, completely amorphous materials to linear, semicrystalline, high-density materials.[2–4]

A great interest in these single site olefin polymerization catalysts has been driven by their ability to produce polyolefinic materials with new or improved performance parameters. In this context, there have been many studies focusing on utilizing these catalysts for the production of new polyolefinic materials or tailoring the characteristics of a specific polymer by employing different polymer blending methods. One method, which is widely used to enhance polymer processibility, involves the production of new polyolefins with broad molecular distribution by physical blending of two or more polymers with different molecular weights.[10,11] Another method involves the use of a series of multi-stage reactors with each operated at different polymerization conditions and thus producing polymers with different properties.[10,12]

The third method for the production of polymer blends, known as reactor blending, involves combining two or more types of catalysts to produce polymers with different and controlled properties in a single reactor.[10] In this method, each catalyst polymerizes ethylene independently, generating different polyethylenes during the polymerization reaction, and thus forming a reactor blend.[10] The simplicity of this method allows the polymer properties to be tai-

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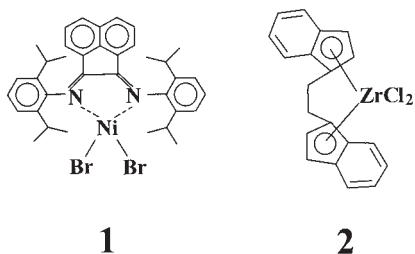
Scheme 1

lored by simple adjustment of the catalyst ratio and polymerization conditions. Recently, a few studies have shown that ethylene polymerization with the combination of metallocene and nickel or iron diimine catalysts produces reactor blends of branched and linear polyethylene.[13–15] The combination of these catalysts showed high activity and gave materials with new properties.

In this article, we report the results of ethylene polymerization using a combination of [1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide] (**1**)/MMAO, known as an active catalyst for the production of branched polyethylene, and [rac-ethylenebis(indenyl) zirconium dichloride] (**2**)/MMAO, known as an active catalyst for the production of linear polyethylene (Scheme 1). The study investigates the effect of molar catalyst fraction of **1** and **2** and polymerization conditions on the catalyst activity and polymer properties. Our investigation explored the performance of the combined catalysts at low as well as high ethylene pressure.

EXPERIMENTAL

Materials

All manipulation involving air and/or moisture sensitive compounds was performed in a dry nitrogen glove box or under ultra pure nitrogen protection. The α-diimine ligand and catalyst precursor [1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide] (**1**) were synthesized following the procedures reported in the literature.[2,3] The zirconocene catalyst precursor, [rac-ethylenebis(indenyl) zirconium dichloride] (**2**), was purchased from Boulder Scientific Company and used as received. The cocatalyst, modified methylaluminoxane (MMAO: with 65.9 mol % methane and 31.7 mol % isobutane) was purchased from Akzo-Nobel Corp. as 7.25 wt % aluminum in toluene. Polymerization-grade ethylene (99.9% purity) was purchased from Matheson Gas and further purified by passing it through CuO, ascarite, and molecular sieves. Anhydrous toluene from Aldrich was refluxed over sodium with benzophenone as indicator and distilled under ultra pure nitrogen atmosphere prior to use.

Polymerization runs

Ethylene polymerization at 6 psig ethylene pressure. The polymerization was carried out in a 500 mL glass reactor equipped with a magnetic stirrer under 6 psig ethylene pressure. Toluene and MMAO were introduced into the reactor under nitrogen protection. The reactor was evacuated, pressurized with ethylene, and then placed into an oil bath set at the operating temperature. After equilibrium for 10 min, a prescribed amount of toluene solution of **1** or **2** was injected to start polymerization. For polymerization with binary catalyst **1**/**2**/MMAO, the prescribed amount of each catalyst (**1** and **2**) solution in toluene was injected simultaneously to initiate the concurrent polymerization. The reaction temperature and ethylene pressure was kept constant throughout the polymerization process. Magnetic stirring was applied. After 0.5 h, the reaction was vented and quenched by injecting 20 mL methanol. The polymer produced was collected, washed with an acidified methanol, and then vacuum dried at 50°C for 16 h.

Ethylene polymerization at 100 psig ethylene pressure. The polymerization runs were carried out in a one-liter Autoclave stainless steel reactor operated in a semibatch mode. The reactor was carefully cleaned with acetone, vacuumed at 150°C for 3 h, and then purged four times with ultra pure nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The required amount of cocatalyst MMAO solution was injected to the reactor under nitrogen atmosphere using gas-tight syringes. The mixture was kept under stirring while the reactor was heated up to establish the desired polymerization temperature. Once the desired temperature was established, the prescribed amount of each catalyst (**1** and **2**) solution in toluene was injected simultaneously to initiate the concurrent polymerization. To start polymerization, the reactor was pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuous feeding of gaseous ethylene to the reactor. The reactor temperature was maintained within ± 1°C of the desired temperature by water/ethylene glycol cooling circulation. The reaction was stopped by rapid depressurization of the reactor, followed by quenching with methanol. The polymer produced was washed with acidic methanol to remove MMAO residue, then filtered and dried under vacuum at 60°C for 16 h.

Polymer characterization

Polymer molecular weight (MW) and molecular weight distribution (MWD) were measured at 140°C in 1,2,4-trichlorobenzene using a Waters Alliance GPCV 2000 with DRI detector coupled with an on-line capillary viscometer. A calibration curve was estab-

TABLE I
Ethylene Polymerization with Binary Catalytic System 1/2/MMAO[a]

Run	Catalyst (X_2)[b]	T (°C)	P (psig)	Time (min)	Activity[c] ($\times 10^{-3}$)	M_w (kg/mol)[d]	PDI[d]	T_m (°C)[e]	ΔH (J/g)[e]	X_c (%)[e]
1	0	5	6	30	1.95	588	2.8	107.6	66	23
2	0.01	5	6	30	1.71	495	2.5	107.4	67	23
3	0.1	5	6	30	2.10	388	2.1	106,112	53	18
4	0.5	5	6	30	1.85	478	2.3	97,112	101	35
5	1	5	6	30	2.30	517	2.3	133	168	58
6[f]	0	30	6	30	2.50	286	2.3	—	—	—
7	0.01	30	6	30	2.95	310	2.7	129	4	1.4
8	0.1	30	6	30	3.87	343	2.9	131	26	9
9	0.5	30	6	30	4.23	328	3.1	134	157	54
10	1	30	6	30	6.21	387	2.3	134	169	58
11[f]	0	50	6	30	1.65	188	2.3	—	—	—
12	0.01	50	6	30	2.10	196	2.8	127	3.4	1.2
13	0.1	50	6	30	4.35	215	3.4	129	114	39
14	0.5	50	6	30	6.23	174	3.5	131	146	50
15	1	50	6	30	10.50	168	2.2	135	172	59
16	0	60	100	15	7.25	145	2.4	50	32.5	11
17	0.01	60	100	15	7.87	125	2.2	49,127	13,21	5,7
18	0.1	60	100	15	7.92	95	2.3	53,128	18,15	6,5
19	0.5	60	100	15	10.50	84	2.7	132	174	60
20	1	60	100	15	14.23	67	2.1	135	189	65

[a] Other reaction conditions: solvent, toluene; volume, 250 ml for runs 1 ~ 15 and 450 ml for runs 16 ~ 20; Al/(Ni+Zr) = 1500 (molar).
[b] X_2 = moles of 2/(moles of 1 + moles of 2).
[c] kg of PE/mol (Ni+Zr) × hr.
[d] Determined by GPCV.
[e] Measured by DSC.
[f] These samples are totally amorphous.

lished using monodisperse polystyrene standards. The DSC analysis was carried out using a Thermal Analysis 2910 instrument from TA Inc. in the standard DSC run mode. Thirty mL/min of ultra pure nitrogen gas was fed continuously to purge the calorimeter. Sample cooling was done using a refrigeration cooling unit attached to the DSC cell. The instrument was initially calibrated for the melting point of an indium standard at a heating rate of 10°C/min. The polymer sample, about 5 mg, was first equilibrated at 0°C, then heated to 180°C at a rate of 10°C/min to remove its thermal history. The sample was then cooled down to 0°C at a rate of 10°C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of catalyst 2 molar fraction (X_2) on overall catalyst activity

We carried out ethylene polymerization at different levels of catalyst fractions, reaction temperatures, and ethylene pressures. Table I gives the results of ethylene polymerization reactions. The activities of the individual catalysts, **1** or **2**, varied depending on the polymerization conditions. At all the polymerization temperatures and pressures, the catalyst system

1/MMAO showed lower activity than **2**/MMAO. With catalyst **1**/MMAO at 6 psig, the catalyst activity increased with the increase of the polymerization temperature from 5 to 30°C but decreased at 50°C due to catalyst deactivation. Contrarily, the activity of **2**/MMAO increased with temperature reaching a maximum value at 50°C. It is also worth noting that increasing reaction temperature increased the difference in the catalyst activities obtained from systems **1**/MMAO and **2**/MMAO. The effect of ethylene pressure on catalyst activity for both catalyst systems is also clear as revealed from the data in Table I. Increasing ethylene pressure from 6 to 100 psig increased the activity of both catalysts because the catalyst active sites were exposed to higher ethylene concentration at higher ethylene pressure.

Figure 1 shows the effects of polymerization temperature, ethylene pressure, and molar fraction of catalyst **2** on the overall catalyst activity. The effect of catalyst **2** molar fraction X_2 on the overall catalyst activity can also be seen clearly from Figure 1. At 5°C, there was very little influence of catalyst **2** molar fraction on the overall catalyst activity. The catalyst activity changed from 1.7 to 1.85 ($\times 10^3$ kg PE/mol hr) when catalyst **2** molar fraction was increased from 0.01 to 0.5. However, variation of the catalyst **2** molar fraction at 30 and 50°C yielded a significant effect on

the catalyst activity. The overall catalyst activity increased linearly with catalyst **2** molar fraction. A linear dependency was also seen for polymerization carried out at 60°C and 100 psig. This linear correlation between catalyst activity and X_2 suggested that interactions between catalyst **1** and **2** species were minimal, and the catalysts performed independently from each other.
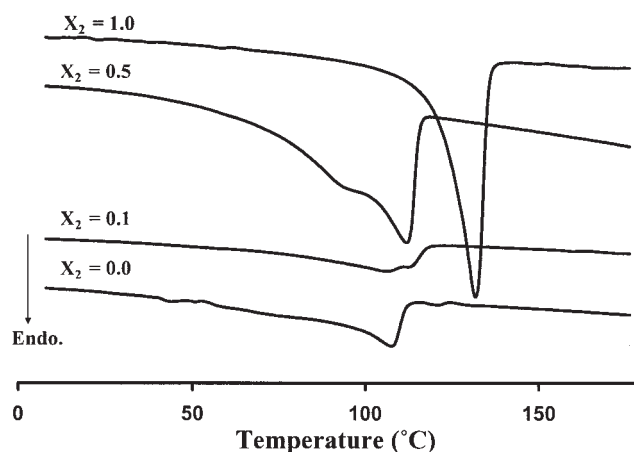
Effect of catalyst 2 molar fraction (X_2) on polymer properties

The effects of X_2, polymerization temperature, and ethylene pressure on the microstructure of the polymers produced were investigated by means of gel permeation chromatography (GPC) for molecular weight analysis and differential scanning calorimetry (DSC) for thermal analysis. We reported the DSC thermal analysis in terms of melting temperature (T_m), heat of fusion (ΔH_m), and degree of crystallinity (X_c). The melting behavior of polyethylene is mainly related to short chain branching. Increasing short chain branching density decreases lamellar thickness of the crystal structure and thus lowers melting temperature of the polymer. The short chain branching also affects the degree of crystallinity, which is proportional to the fractional amount of crystalline phase in the polymer sample.

It is known that catalyst **1**/MMAO will homopolymerize ethylene to produce branched polyethylene, and the degree of branching increases with polymerization temperature.[2–4] As shown in Table I, at 5°C, catalyst **1**/MMAO produced branched polyethylene with T_m = 107.6°C and X_C = 23% (run 1), and catalyst **2**/MMAO produced linear polyethylene with T_m = 133°C and X_C = 58% (run 5). As revealed from Table I, it is also clear that the melting behavior of the polymer sample produced at 5°C was affected by changing the catalyst **2** molar fraction. For example,
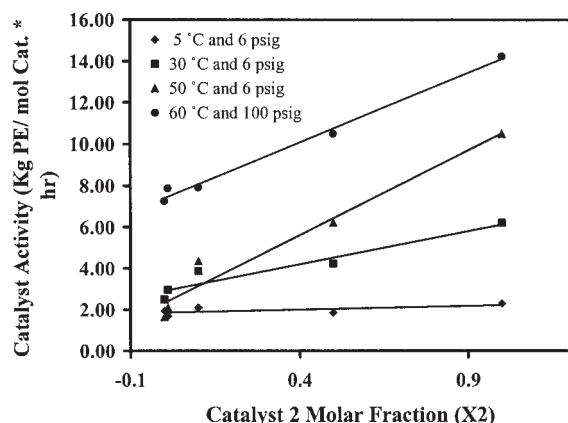
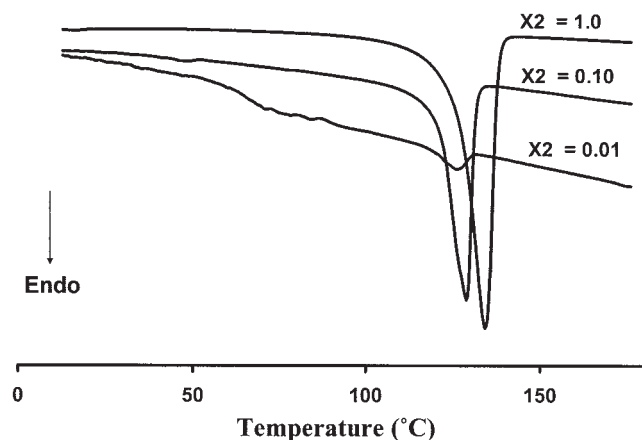**Figure 1** Effect of temperature, pressure, and X_2 on catalyst activity.

Figure 2 DSC thermograms for polymers produced with **1**/**2**/MMAO system at 5°C and 6 psig: effect of X_2 on polymer melting behavior.

increasing the catalyst 2 molar ratio from X_2 = 0.1 (run 3) to X_2 = 0.5 (run 4), the polymer crystallinity was increased from X_C = 18% to X_C = 35%. This increase in the crystallinity was due to the increase of the linear polymer amount as we increased X_2. The DSC thermograms in Figure 2 show that at X_2 = 0.1 and X_2 = 0.5, both low and high melting peaks were shifted to lower temperatures compared to the melting peaks of the polymers produced with the individual catalysts. This observation probably suggests that there is a sort of competition and interference during the crystallization of both branched and linear polyethylene.

In contrast, at 30 and 50°C, the polymers produced with the catalyst **1**/MMAO system were totally amorphous due to high branching, and therefore a different melting behavior was observed. At such conditions, the polymers produced with the binary catalyst system were mixtures of amorphous PE from catalyst **1**/MMAO and semicrystalline PE from catalyst **2**/MMAO. Therefore, there might be little interference and competition between both polymers during the crystallization process. Figure 3 shows the melting behavior of the polymer samples produced at 50°C and different values of X_2. The DSC thermogram shows only single peaks of the crystalline polymers produced by catalyst **2**. As shown in Table I, it is also clear that increasing X_2 had a strong effect on the polymer crystallinity. For example, for the polymerization runs held at 50°C, increasing the catalyst **2** molar ratio from X_2 = 0.01 to X_2 = 0.5, the polymer crystallinity was increased from X_C = 1.2% to X_C = 50.

It is known that ethylene pressure has a remarkable effect on the microstructure of polyethylene produced with catalyst **1**/MMAO.[4–9] In an attempt to understand the effect of ethylene pressure on the characteristics of the polymer produced with **1**/**2**/MMAO, ethylene polymerization runs were carried out at 60°C

Figure 3 DSC thermograms for polymers produced with $1/2$/MMAO system at 50°C and 6 psig: effect of X_2 on polymer melting behavior.

and 100 psig. At such conditions, **1**/MMAO produced branched polyethylene with $T_m = 50°C$ and $X_C = 11.2\%$ (run 16), and catalyst **2**/MMAO produced linear polyethylene with $T_m = 135°C$ and $X_C = 65\%$ (run 20). As revealed from the DSC data (Fig. 4), the melting curves of the polymers produced with **1/2**/MMAO exhibited two distinct peaks with melting temperatures closely corresponding to those of the polymers produced with the individual catalysts, **1**/MMAO and **2**/MMAO. This observation suggested that the interference between both polymers was minimal during the crystallization process due to the big difference in the melting temperatures of the polymers produced with the individual catalysts. It also suggested that when running **1/2**/MMAO at high ethylene pressure, each individual catalyst behaved independently towards ethylene polymerization.

At 5°C, the polyethylene samples produced with the catalyst systems **1**/MMAO and **2**/MMAO exhibited comparable weight average molecular weight of 588 kg/mol and 517 kg/mol, respectively. The polyethylene samples produced at various catalyst **2** molar fractions ($X_2 = 0.01$, 0.1, and 0.5) showed a slight reduction in M_w with a monomodal molecular weight distribution and narrow polydispersity.

When polymerization temperature was increased to 30°C or 50°C, the weight average molecular weights were reduced for the catalyst systems of **1**/MMAO and **2**/MMAO. This reduction in M_w for both catalysts was attributed to the enhancement of the chain transfer rate as we increased the polymerization temperature. As shown in Table I, at 30°C or 50°C, the polyethylene samples produced with $X_2 = 0.1$ and 0.5 showed monomodal molecular weight distribution with slight broadness. For example, the polyethylene produced at 50°C and $X_2 = 0.5$ showed polydispersity of 3.5, in comparison to polydispersities of 2.3 and 2.2 for the polymers produced with the individual catalysts, **1**/MMAO and **2**/MMAO, respectively.

At higher temperature and ethylene pressure (60°C, 100 psig), the polyethylene produced showed far lower molecular weight than those produced at 6 psig and various polymerization temperatures and catalyst fractions. Similarly, the polymer produced showed monomodal molecular weight distribution and narrow polydispersities.

CONCLUSION

We demonstrated the synthesis of different reactor blends of linear and branched ethylene homopolymers by combining catalysts **1** and **2** at various polymerization conditions. At 5°C and 6 psig, there was little influence of the catalyst **2** molar fraction on the overall catalyst activity. At higher temperatures of 30 and 50°C, a linear correlation between the overall catalyst activity and X_2 indicated that the interactions between the catalyst **1** and **2** species were minimal, and the two catalysts performed independently. At 60°C and 100 psig, a similar linear correlation was observed. For the polyethylene produced at 5°C and $X_2 = 0.5$, the DSC thermograms showed bimodal peaks with melting points shifted to lower temperatures compared to those of the polymers produced with the individual catalysts, suggesting that there was a sort of competition and interference during the crystallization of both branched and linear polyethylenes. At 30 and 50°C, the polymer produced with the binary catalyst system was a mixture of amorphous PE from catalyst **1** and semicrystalline PE from catalyst **2**. This resulted in less interference and competition between both polymers during the crystallization process, thus leading to DSC curves with single melting peaks coming from the catalyst **2** polymer. At 60°C and 100 psig, the DSC thermograms of the polymers produced with **1/2**/MMAO exhibited two distinct peaks with melting temperatures closely correspond-
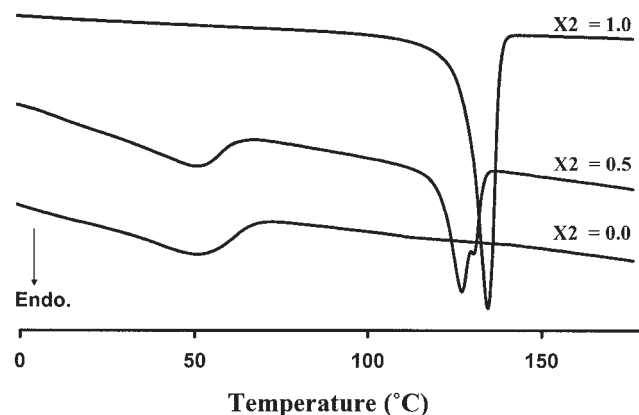
Figure 4 DSC thermograms for polymers produced with $1/2$/MMAO system at 60°C and 100 psig: effect of X_2 on polymer melting behavior.

ing to the melting temperatures of the polymers produced with the individual catalysts, **1**/MMAO and **2**/MMAO. The GPCV analysis for all the produced polyethylene samples showed monomodal molecular weight distributions with low polydispersities.

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