Copolymerization of Ethylene and 1-Hexene Catalyzed by the Zirconocene/ $\text{Al}(i\text{-Bu})_3/\text{B}(\text{C}_6\text{F}_5)_3$ Catalytic System

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Abstract: Copolymerizations of ethylene/1-hexene were conducted using different zirconocene/ $\text{AlR}_3/\text{B}(\text{C}_6\text{F}_5)_3$ catalytic systems at 50 °C. When AlEt_3 was used as alkylate agent, very low copolymerization activity was observed with both bridged catalyst $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ and unbridged zirconocene Cp_2ZrCl_2 in-situ activated with $\text{B}(\text{C}_6\text{F}_5)_3$. In appropriate Al/Zr mole ratio using $\text{Al}(i\text{-Bu})_3$, the catalytic activities of both zirconocene catalytic systems were similar to those of sophisticated zirconocene/methylaluminoxane(MAO) catalytic system. The catalytic activities, comonomer incorporation and molecular weight of the copolymer synthesized with $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{B}(\text{C}_6\text{F}_5)_3$ were higher than those obtained with $\text{Cp}_2\text{ZrCl}_2/\text{Al}(i\text{-Bu})_3/\text{B}(\text{C}_6\text{F}_5)_3$. The effect of the concentration of 1-hexene on catalytic activity, copolymer molecular weight, and comonomer incorporation was investigated. The complicated “co-monomer effect”, together with an increase in comonomer incorporation, a decrease in the copolymer molecular weight, was found when the comonomer concentration was increased.

Introduction

Linear low-density polyethylene (LLDPE) synthesized by copolymerization of ethylene with α -olefins such as 1-butene, 1-hexene, 1-octene, is an important class of polymer because of its specific properties, for example, offering better impact and film tear properties than high-density polyethylene (HDPE) and a balance of toughness and stiffness [1, 2]. LLDPE synthesized using traditional Ziegler–Natta catalysts produce polymers with a wide molecular weight distribution (MWD, M_w/M_n) and chemical composition distribution (CCD) because of multiple active sites [3, 4]. In contrast, homogeneous metallocene catalysts for olefin polymerization present an opportunity for better control of polymerization behavior, structure and properties of the resulting polymer over the traditional Ziegler–Natta catalysts owing the single-site nature and produce very uniform polymers with narrow MWDs and CCDs [5-11]. Many contributions have been made concerning this topic, and almost all of them have been performed on sandwiched transition metal main catalyst. On the other hand, very few examples about the role of co-catalyst on production of LLDPE are described in the literature.

As it is well known, co-catalysts are generally used to activate the single-site metallocene catalysts by forming ion pairs which are the active agents for olefin polymerization. The co-catalyst, which becomes an anion after the activation process, is the vital part of a catalytically active cation-anion ion pair and may significantly influence polymerization characteristics and polymer properties [12]. The

most commonly used co-catalysts are methylaluminoxane (MAO). However, it must be used in large excess (1000–10 000 eq. per eq. of transition metal) to reach optimum catalyst activity, thus generating a significant part of the total cost of the catalyst, moreover, the structure of MAO are still not entirely clear or well understood. The search for alternative, simple activators started early on in metallocene catalyst research, together with the understanding of their cationic nature. Organo-Lewis acid cocatalysts such as perfluoroarylboranes $B(C_6F_5)_3$, or borate salts, for example $[Ph_3C][B(C_6F_5)_4]$ or $[PhNHMe_2][B(C_6F_5)_4]$, can be used as stoichiometric cocatalysts in olefin polymerization with a large number of alkylated organometallic complexes, such as dimethylzirconocenes [13, 14]. Unfortunately, dimethyl zirconocenes is unstable; many works reported about ethylene homo-polymerization through a efficient and convenient ternary system comprised of $L_2ZrCl_2/Al(i-Bu)_3/B(C_6F_5)_3$ (L : ligands) [15-17]. Here, we report the copolymerization behavior of ethylene with 1-hexene using these ternary catalytic systems.

Results and discussion

Catalytic activity

Two different alkylaluminum, $AlEt_3$ and $Al(i-Bu)_3$ were employed as alkylate agent for zirconocene in catalytic copolymerization of ethylene/1-hexene. The results are summarized Table 1.

Tab. 1. Ethylene copolymerization with 1-hexene catalyzed by $Et(Ind)_2ZrCl_2/Al(i-Bu)_3/B(C_6F_5)_3$.^a

Run	AlR_3	Al/Zr	Activity ^b
1	$Al(i-Bu)_3$	50	1.2
2	$Al(i-Bu)_3$	100	3.9
3	$Al(i-Bu)_3$	200	5.5
4	$Al(i-Bu)_3$	300	1.8
5	$Al(i-Bu)_3$	400	1.2
6	$AlEt_3$	50	-
7	$AlEt_3$	100	-
8	$AlEt_3$	200	trace
9	$AlEt_3$	300	trace
10	$AlEt_3$	400	-

^aPolymerization condition: $[Zr]=[B]=1 \times 10^{-5} M$, $T_p=50\text{ }^\circ C$, $t=30\text{ min}$, 50 mL toluene

^bPolymerization activity: $10^6\text{ g of the Polymer/molZr.h.atm}$

It is found that the effect of aluminum compounds on the activities of copolymerization were crucial under otherwise identical conditions. For $AlEt_3$, there were fewer copolymers obtained at any concentration of $AlEt_3$. For $Al(i-Bu)_3$, the activities of copolymerization depend on the concentration of $Al(i-Bu)_3$, the maximum activity can be reached with Al/Zr molar ratio of 200; this can be attributed to the

different active center formation as previous discussed in ethylene homo-polymerization [17].

The results of copolymerization with different 1-hexene concentration and different zirconocene when using $\text{Al}(i\text{-Bu})_3$ as alkylate agent are summarized in Table 2. It is found that, the activity of ethylene/1-hexene copolymerization increases with increasing 1-hexene feed concentration up to 0.2 M compared with that of ethylene homo-polymerization irrespective of the main catalyst being Cp_2ZrCl_2 or $\text{Et}(\text{Ind})_2\text{ZrCl}_2$.

Tab. 2. Ethylene copolymerization with 1-hexene catalyzed by zirconocene/ $\text{Al}(i\text{-Bu})_3/\text{B}(\text{C}_6\text{F}_5)_3$.^a

Run	Zirconocene	1-Hexene (M)	Activity ^b	1-Hexene incorporation ^c
1	Cp_2ZrCl_2	0	2.6	0
2	Cp_2ZrCl_2	0.1	3.4	4.8
3	Cp_2ZrCl_2	0.2	2.8	7.6
4	Cp_2ZrCl_2	0.4	2.4	14.1
5	Cp_2ZrCl_2	0.6	2.1	15.9
6	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	0	3.0	0
7	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	0.1	3.5	7.3
9	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	0.2	5.5	12.5
9	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	0.4	2.9	20.6
10	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	0.6	2.2	22.4

^aPolymerization conditions: $[\text{Zr}]=[\text{B}]=1\times 10^{-5}\text{M}$, $T_p=50^\circ\text{C}$, $t=30\text{min}$, 50 mL toluene

^bPolymerization activity: $10^6\text{g of the Polymer/molZr.h.atm}$

^cMolar content (%) estimated by ^{13}C NMR

The activity decreases with increase of 1-hexene feed concentration, when the initial 1-hexene concentration was increased from 0.2M to 0.4M. This can be attributed to the so-called “co-monomer effect” that has been thoroughly studied by many researchers, and was found in ethylene copolymerization with α -olefin (propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) in almost all metallocene catalysts. Many researchers believe that this is due to the physical effects and the chemical effects [20-22]. The first is that the co-monomer unit incorporated into the polymer chain influences the solubility of the polymer, thereby the resistances of the monomer transfer and the heat transfer would be reduced. The second effect is that the introduction of the co-monomer can influence the catalytic active species. In this case, the coordination of the co-monomer to the active species may stabilize the cationic active species, as the result of that the co-monomer always possesses a stronger electron donating ability than ethylene. On the other hand, the rate of the bulkier co-monomer insertion into the propagation chain is always much slower than that of ethylene because of the steric hindrance.

$[Zr]=[B]=1 \times 10^{-5} M$, $Al/Zr=200$, $T_p=50^\circ C$, 50 mL toluene, $t=30min$

Fig. 1. Kinetic curve of ethylene/1-hexene copolymerization catalyzed by $Cp_2ZrCl_2/Al(i-Bu)_3/B(C_6F_5)_3$ catalytic system.

$[Zr]=[B]=1 \times 10^{-5} M$, $Al/Zr=200$, $T_p=50^\circ C$, 50 mL toluene, $t=30min$

Fig. 2. Kinetic curve of ethylene/1-hexene copolymerization catalyzed by $Et(Ind)_2ZrCl_2/Al(i-Bu)_3/B(C_6F_5)_3$ catalytic system.

The observation of activity profile is the combination of these effects, based on the nature of the catalyst and the polymerization condition. At low co-monomer

concentration, an enhancement in activity resulted from the solubility of the polymer. At the higher 1-hexene concentration, the activity decreased as a result of the increased probability of coordination and insertion of 1-hexene, therefore the steric effect and, in particular the lower propagation chain constants involving 1-hexene insertion, depressed the overall polymerization rate.

Under the same polymerization conditions, comparing both catalysts, $\text{Et(Ind)}_2\text{ZrCl}_2$ and Cp_2ZrCl_2 , $\text{Et(Ind)}_2\text{ZrCl}_2$ was shown to be the most active. This should be attributed to the bigger bite angle of the bridged catalyst which makes 1-hexene coordination and insertion easier. On the other hand, the lower positive charge density of transition metal of $\text{Et(Ind)}_2\text{ZrCl}_2$ also benefit 1-hexene coordination. As a whole, the two in-situ zirconocene catalytic systems showed high activity for ethylene/1-hexene copolymerization similar to that zirconocene/MAO catalytic system. The polymerization behavior is strongly dependant on the chosen catalyst. The kinetic profile in Figure 1 and Figure 2 show that the higher R_p was reached in less than 3 min, revealing that during the first moments of the reaction practically all the catalytic sites were already formed. However, there was a strong reduction in R_p after the minutes of polymerization.

Molecular weight and microstructure of the result copolymer

The GPC curve of the resultant copolymers using different catalytic system is shown in Figure 3. The molecular weight and MWD are summarized in Table 3. It reveals that the molecular weight of the obtained copolymers is much higher than that obtained from zirconocene/MAO catalytic system [23]. The molecular weight of resultant polymers decreased with an increase in the 1-hexene concentrations feed using both catalytic systems. Obviously, the β -H elimination and chain transfer reaction occur more readily with the increasing 1-hexene concentrations.

Fig. 3. GPC curve of ethylene/1-hexene copolymer resulted from zirconocene/ $\text{Al}(i\text{-Bu})_3/\text{B}(\text{C}_6\text{F}_5)_3$ catalytic system.

Tab. 3. Molecular weight and its distribution of ethylene/1-hexene copolymer.

Run	Catalyst	Concentration of comonomer (M)	M_w ($\times 10^{-3}$)	M_w/M_n
1	Cp_2ZrCl_2	0.1	72.6	2.3
2	Cp_2ZrCl_2	0.2	6.3	2.2
3	Cp_2ZrCl_2	0.4	4.8	2.2
4	Cp_2ZrCl_2	0.6	3.4	1.9
5	$Et(Ind)_2ZrCl_2$	0.1	336	2.9
6	$Et(Ind)_2ZrCl_2$	0.2	114.4	2.6
7	$Et(Ind)_2ZrCl_2$	0.4	84.7	2.5
8	$Et(Ind)_2ZrCl_2$	0.6	41.4	2.1

Polymerization conditions: $[Zr]=[B]=1 \times 10^{-5} M$, $T_p=50^\circ C$, $t=30 min$, 50 mL toluene

Tab. 4. Chemical shift assignment in ^{13}C -NMR spectra of ethylene/1-hexene copolymer.

Region	Carbon	Sequence	Chemical [H]=17.3%	Shift [H]=1.9%	Peak No.
A	$\alpha\alpha$	HHHH	41.40		1
	$\alpha\alpha$	HHHE	40.86		2
	$\alpha\alpha$	EHHE	40.18		3
B	CH	EHE	38.13	38.14	4
C	CH	HHE	35.85		5
	4B	HHH	35.37		6
	$\alpha\gamma$	HHEH	35.00		7
	$\alpha\gamma$	EHEH	35.00		
	$\alpha\delta$	HHEE	34.90		8
	4B	HHE	34.90		
	$\alpha\delta$	EHEE	34.54	34.53	9
	4B	EHE	34.13	34.13	10
	CH	HHH	33.47		11
D	$\gamma\gamma$	HEEH	30.94		12
	$\gamma\delta$	HEEE	30.47	30.47	13
	$\delta\delta$	(EEE) $_n$	29.98	29.99	14
	3B	EHE	29.51		15
	3B	HHE	29.34		16
	3B	HHH	29.18		17
E	$\beta\delta$	EHEE	27.28	27.28	18
	$\beta\delta$	HHEE	27.09		19
F	$\beta\beta$	EHEHE	24.53	24.53	20
	$\beta\beta$	HHEHE	24.39		21
	$\beta\beta$	HHEHH	24.25		22
G	2B	EHE+HHE+HHH	23.37	23.36	23
H	1B	EHE+HHE+HHH	14.12	14.12	24

For a polyolefin made with single-site catalysts, the expected theoretical MWD is equal to 2, as described by Flory's probable distribution. Table 3 shows that the MWD of results copolymer is slightly higher than 2, and this implied that the characteristics of the active site is complex due to the in-situ active reaction. Moreover, it was observed in Table 3, the molecular weight of the copolymer produced by $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ catalyst are higher than those of copolymer produced by Cp_2ZrCl_2 catalyst respectively, this also could be explained from the electronic effect of the active site. It is believed that the fluidity of π electron in Indene is easier than Cp ring, the Lewis acidic of the transition metal of bridged catalyst $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ is much weaker than that of Cp_2ZrCl_2 . So that the reaction ability of β -H elimination and chain transfer reaction should be decreased when bridged catalyst $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ employed resulted in the higher molecular weight copolymer.

Copolymer compositions were determined by ^{13}C NMR spectroscopy, typical ^{13}C NMR spectra of the copolymer is presented in Figure 4. The assignment of all peaks was carried out according to the literature [24], as shown in Table 4. The ^{13}C NMR analyses also shows that $\text{Et}(\text{Ind})_2\text{ZrCl}_2 / \text{Al}(\text{i-Bu})_3 / \text{B}(\text{C}_6\text{F}_5)_3$ catalytic system catalyst possesses better incorporation ability than that of $\text{Cp}_2\text{ZrCl}_2 / \text{Al}(\text{i-Bu})_3 / \text{B}(\text{C}_6\text{F}_5)_3$ catalytic system.

Fig. 4. ^{13}C -NMR spectra of ethylene/1-hexene copolymer.

Experimental part

Materials

All the operations were carried out under a dry argon atmosphere with standard Schlenk techniques. Toluene was purified by refluxing over Na/benzophenone under argon atmosphere and distilled prior to use. Methylaluminoxane (MAO, 10% solution in toluene; Albemarle) is commercially available and was used as received. 1-hexene was purified via refluxing over solid sodium under argon and stored in the presence of activated 4-Å molecular sieves. Cyclopentadiene (Cp) was obtained through the

cracking of dicyclopentadiene under an argon atmosphere, Cp_2ZrCl_2 , $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ was synthesized according to the literature [18]. $\text{B}(\text{C}_6\text{F}_5)_3$ was synthesized according to the literature [19]. Polymerization-grade ethylene was further purified by passage over 4-Å molecular sieves.

Ethylene copolymerization

The polymerization was carried out in a 100 mL 3-necked flask equipped with ethylene inlet, magnetic stirrer and vacuum line. After 50 mL toluene was added to the reactor, the solvent was saturated with an atmospheric pressure (0.1 MPa) of ethylene at the required temperature. Calculated amounts of 1-hexene, AlR_3 , zirconocene and $\text{B}(\text{C}_6\text{F}_5)_3$ solution in toluene were added in this order. Ethylene consumption was recorded by a device composed of an electromagnetic valve and a pressure sensor which maintain polymerization pressure at 0.1 MPa. After 30 min, the polymerization was terminated by addition of acidified ethanol. The resulting polymer was separated by filtration and dried under vacuum at 60 °C till constant weight.

Polymer characterization

The ^{13}C NMR spectra of the copolymers were obtained in a Bruker Avance-DMX 500 NMR apparatus in o-dichlorobenzene at 130 °C. Molecular weight and molecular weight distribution was measured at 130 °C by gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene as eluent using polystyrene standards for reference.

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