Copolymerization of Ethylene with α−olefins using synthesized BisIndZrCl$_2$ Metallocene catalyst

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Abstract

BisIndZrCl$_2$ catalyst was synthesized according to classic method. The copolymerization of ethylene with different α−olefin (1-hexene and 1-octene) was studied using the catalyst. The activity of the catalyst decreases as the comonomer concentration increases and the obtained rate/time profiles show this catalyst has decay type behavior for both homopolymerization and copolymerization. The terms of comonomer effect factor (CEF) and decay index (DI) were investigated. The observed results of CEF and DI indicate that a rate depression effect has happened in this homogeneous catalytic system.

Keywords: Metallocene catalyst- Copolymerization - Ethylene– α-olefin Copolymer- Comonomer

Introduction

As one of the olefin polymerization metallocene catalysts have been at the center of the attention in the past decade and their importance have been increase as new catalysts to produce polymers with unique properties [1-3]. In Comparison with Ziegler-Natta catalysts, metallocene catalysts can control the polymer properties much better. Also incorporation of α-olefins in ethylene copolymerization using metallocene catalysts are better and have higher activity, too[4,5] There have been many efforts toward finding suitable catalysts for copolymerization of α−olefins and studying the kinetic behavior[6,7]. In this work the influence of comonomer concentration on performance of catalyst was investigated.

Experimental
Material

All operations were carried out in dry nitrogen. Indene (90%), 1-Hexene and 1-Octene were brought from Merck and MeLi solution in Et$_2$O was purchase from Acros. MAO (10%wt in toluene) was denoted by Aldrich. Toluene, Et$_2$O, Pentane and CH$_2$Cl$_2$ were purchase from Luba (India) and all of them were refluxed and distilled over drying agent before use.

Catalyst Synthesis

MeLi (9.9 ml of a 1.6 M solution) was added drop wise to Indene (1.97 gr) dissolved in Et$_2$O (30 ml). At the end of the addition, the mixture was stirred for 40 min at room temperature (r.t). The mixture was added at once to ZrCl$_4$ (7.9 mmol, 1.84 gr) dispersed in pentane (30 ml). Suspension was stirred for 2 h at 25 $^{\circ}$C. The product was filtrated and the residue was dried and extracted at reflux using CH$_2$Cl$_2$ (80 ml) for at least 5 h, the extract was dried to give Ind$_2$ZrCl$_2$ catalyst.

Copolymerization

Ethylene copolymerization was performed in 450 ml toluene in a 1 lit Buchi reactor that connected to constant temperature circulator. Toluene was introduced in to the reactor and saturated with 1 atm ethylene at the required temperature. The polymerization components were added in the following orders; MAO, the comonomer and the catalyst solution. After 1 h reaction, the polymer was poured into an excess amount of methanol, filtered and dried.

Result & Discussion
Copolymerization

Copolymerization of ethylene with 1-hexene and 1-octene were carried out. Table 1 and Table 2 show the catalytic behavior of the bisIndZrCl$_2$ and physical properties of the obtained copolymers. Figure 1 shows the rate/time profiles for the

copolymerization. The profiles are of decay types for both homopolymerization and copolymerization. In metallocene type catalysts usually a low enhancement factor has been reported for small molecule α–olefins such as 1-butene, whereas rate depression has been reported for longer α–olefins such as 1-hexene and 1-octene [5,8]. The term comonomer effect factor (CEF) is defined as $Rp_{av}(co)/Rp_{av}(hom)$ and decay index (DI) is the extent of decrease in catalytic activity at the end of the polymerization reaction which define as $(Rp_{(max)}/Rp_{(min)}$, for 60 min polymerization) (Table 1 and Table 2). The observed results of CEF<1 and DI >>1 indicates that a rate depression effect has happened in this homogeneous catalytic system. The negative trend observed for CEF in copolymerization can be attributed to a competitive coordination of the comonomer to the active center resulting in a possible deactivation of some catalytic centers [5,8]. The CEF also decreased with increasing the molar mass of the comonomer used.

Conclusion

In the study comparative activity of bis-IndZrCl$_2$ catalyst for copolymerization of ethylene with 1-hexene and 1-octene was investigated. The following conclusions were obtained:

- Addition of comonomer 1-hexene and 1-octene, decreased polymerization activity.
- The (CEF) and (DI) both were decreased with addition of the comonomers.

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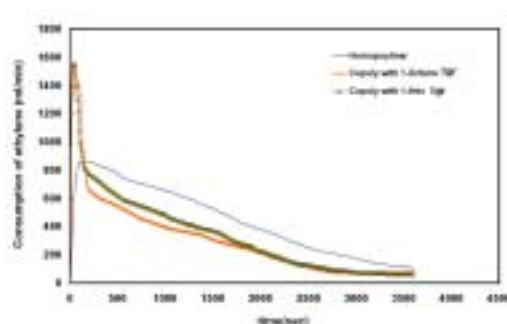8. J. A. M. Awudza, P.J.T. Tait, J. Polym. Sci. Part A:Polym. Chem. **46**, 267, 2008.

Fig. 1 Profile of Rate vs time for copolymeriztion ethylene/1-hexene and 1-Octene, conditions: temp= 60 ^{o}C, monomer pressure = 4 bar, [Al]/[Zr]= 4000:1, toluene= 450 ml, [Cat]= 1.0*10^{-6} mol Zr.

Table 1. Catalytic behavior and physical properties of ethylene/1-hexene copolymer.

1-hexene (gr)	Activity$^{.a}$	CEF	DI
0	3.3 *10^4	1.00	8.6
1	2.5 *10^4	0.78	25.9
2	2.0 *10^4	0.61	32.2
4	0.7 *10^4	0.22	25.4

Conditions: same as Fig. 1
a) Activity: kg Polymer/ mol Zr.hr.

Table 2. Kinetic parameters and physical properties of ethylene/1-octene copolymer.

1-Octene (gr)	Activity^a	CEF	DI
0	3.3 *10^4	1.00	8.6
1	1.9 *10^4	0.59	22.1
2	0.7 *10^4	0.20	33.0
4	0.1 *10^4	0.03	---

Conditions: same as Fig. 1
a) Activity: kg Polymer/ mol Zr.hr.