Polymerization of Ethylene Using Cp₂ZrCl₂ Metallocene and Methylaluminoxane Homogeneous Catalyst System

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A B S T R A C T

Bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) as a homogeneous metallocene catalyst was manufactured in laboratory scale under highly controlled conditions. Ethylene polymerization was carried out using this catalyst while, methylaluminoxane (MAO) was used as a cocatalyst. Activity of 5759 gPE/mmol Zr.h at [Al]/[Zr] molar ratio of 770/1 was obtained. Polymer yield was increased with increasing in [Al]/[Zr] ratio to a limiting value. Addition of hydrogen as a chain transfer agent up to 120 cm^3/L solvent, increased the activity of the catalyst. Polymerization was carried out at monomer pressure of 1 to 5 atm, and temperature of 40°C to 80°C. Polymerization activity was increased with increasing temperature to 60°C and slightly decreased with more increase in temperature. Upon the addition of catalyst a sudden increase of 10°C in temperature was observed, particularly when polymerization temperature was higher than 50°C. This increase could be due to high rate of polymerization which at high temperature could affect catalyst activity. Monomer pressure up to 2 atm increased productivity of catalyst. Increase in [Al]/[Zr] ratio, polymerization temperature and H_2 concentration decreased $\overline{M}_v$ of polymer obtained. Melting point of polymer also decreased with increasing [Al]/[Zr] ratio. Density of obtained polyethylene was 0.940-0.950 g/cm^3. T_g of one of the polymer samples was determined which was 99.9°C.

INTRODUCTION

Polymerization of olefins to polymers with different microstructures and properties is one of the most investigated areas in both industrial and academic laboratories in polymer science [1,2]. The use of polyolefins as polymer is rapidly growing and reaches a production level of million tones a year [3]. In this filed, metallocene catalysts have become increasingly important as part of potentially new generation of Ziegler-Natta (ZN) catalyst. As an advantage over the conventional ZN

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catalyst, metallocene or single site catalyst have the capability of better control of polymer tacticity, molecular weight, and molecular weight distribution [4-6].

Metallocene catalysts consist mainly of compounds of group IV of transition metals (Ti, Zr, Hf) and a cocatalyst of aluminium compounds. Among them, zirconium compounds are the most active and common catalyst which are studied [1-3,7-10]. At higher temperature zirconium catalysts are more stable and active than titanium or hafnium systems [4].

While development of highly active metallocene polymerization catalyst systems has been one of the major achievements in polymerization catalysis, success in this area has been achieved mostly by discoveries of suitable cocatalyst activation systems. The activation system is AlMe$_3$-H$_2$O (alkylaluminoxane) instead of the traditional one (Al(C$_2$H$_5$)$_3$ or Al(C$_2$H$_5$)$_2$Cl) that was used before.

The most active cocatalyst is methylaluminoxane (MAO), which is obtained by controlled hydrolysis of trimethylaluminum. The cocatalyst is oligomeric compounds of general formula of [-Al(Me)O-]$_n$. The structure of MAO is complicated, which is supposed to be a cage with formula of Al$_{16}$O$_{12}$(CH$_3$)$_{24}$ [11]. There is at least one bridging oxo group between two aluminum atoms. Unfortunately homogeneous metallocene catalysts require a large excess of MAO to reach this maximum catalytic activity, which to some extent may impair this value in commercial application [12]. To overcome this problem it should be:

1) Use of cationic metallocene compounds that do not need any cocatalyst for polymerization [5, 13,14].

2) Use of supporting catalysts or co-catalysts by using either inorganic compounds such as Al$_2$O$_3$, SiO$_2$, MgCl$_2$ [5,10,15-17], or polymeric materials which may get great attention in industry and academic research [7,10,17]. The amount of MAO that is needed to rich to the maximum activity of supported catalysts is reduced [7,10, 16,17].

Ethylene polymerization behavior is heavily influenced by size and electronic properties of substituents groups on ligands. Electroreleasing groups favor higher activity, but bulky substitunet and withdrawing groups reduce the activity of the catalyst. Aging of the catalyst, type of solvent, and additives also affect ethylene homopolymerization [10]. In ethylene polymeriza-

tion also much work has been done to minimize the [Al]/[Zr] ratio. So Cp$_2$ZrCl$_2$ is one of the most active catalyst [2,18], which is studied in this work.

EXPERIMENTAL

Cp$_2$ZrCl$_2$ catalyst was prepared according to method obtained from literature and developed in Polymer and Petrochemical Institute of IRAN [11]. The starting material was ZrCl$_4$ (anhydrous 98% Merck). MAO was prepared from Aldrich, (10% solution in toluene).

Polymerization runs were carried out in a 1L stainless steel reactor of Buchi (bmd 300) in dry toluene (500 mL). The toluene was refluxed inside the reactor (under vacuum) for about 60 min before the start of each run. The catalyst components were introduced under nitrogen [19-21].

Viscosity average molecular weight ($\overline{M}_v$) was determined [22,23]. Ubbelohde viscometer with a heating jacket , designed and constructed in Iran Polymer and Petrochemical Institute (IPPI) used for determining the $\overline{M}_v$ of polyethylene.The viscometer jacket was heated with boiling chlorobanzene (b.p=131.6^{o}C). Viscosity average molecular weights of samples were obtained with Mark Houwink equation:

$$\eta = KM^{\alpha}$$

Where K=6.77 10^4 and α = 0.64 are constants related to polymer and measuring condition. Decaline is used as solvent. The data for $\overline{M}_v$ determination have been the average of three data.

Melting point of the polymer was determined using DSC PL Model STA 780. T$_g$ of polymer was determined using DMTA PL model. Density of polymer were determined using persisa balance with densitometer facility.

RESULTS AND DISCUSSION

Cp$_2$ZrCl$_2$ catalyst was prepared using ZrCl$_4$ as starting compound. FTIR spectroscopy (FTIR, BRUKER model IFS 48) was used for identification of the catalyst structure (Figure 1). Absorption bonds at 1439 cm^{-1} (s), 1018 cm^{-1} (s) and 806 cm^{-1} (vs) are belonging to ν (C-
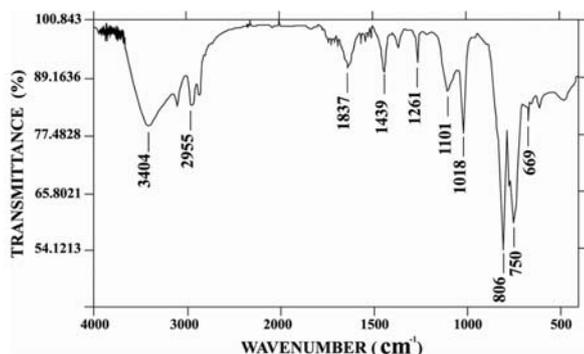
Figure 1. FTIR spectrum of Cp$_2$ZrCl$_2$ catalyst using KBr method.

Figure 2. Plot of average rate of polymerization versus [Al]/[Zr] ratio. Polymerization conditions are as detailed in Table 1.

C) asymmetric in a inplane skeletal, δ (C-H) asymmetric inplane deformation, and δ (C-H) symmetric out of plane deformation, respectively, reported for the same compound [24,25].

Ethylene polymerization was studied at constant Zr concentration and various amounts of MAO. Toluene (500 mL) was used as diluent. The effect of [Al]/[Zr] ratio on polymerization activity, melting point, and $\overline{M}_v$ of the obtained polymer were investigated (Table 1). The influence of the MAO concentration on the rate of ethylene polymerization shows the increasing indicate polymerization activity with increase in the [Al]/[Zr] ratio to a constant value (Figure 2). This behaviour is common for methallocene catalysts [18].

Results of temperature s influence on the polymer yield were presented in Table 2. The catalyst system showed polymerization activity over the whole studied temperature range. However, a slight decrease in activity was observed for temperature higher than 60°C. Upon the addition of the catalyst, a sudden 10°C increase in temperature was observed. The increase was higher particularly when polymerization was carried at higher than 50°C. This behaviour could be the
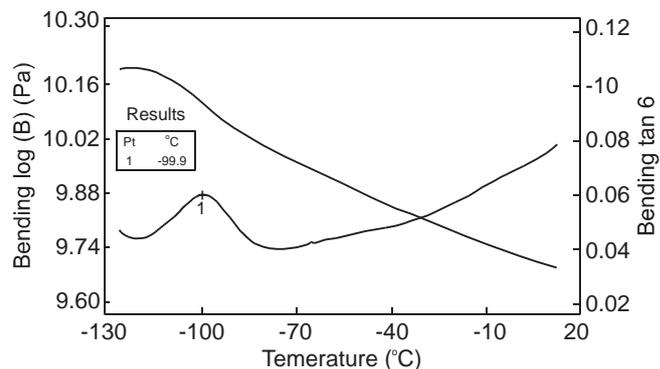
result of decrease in activity at higher temperature than 60°C. The decrease in activity could be due to dissociation of π-olefin complex [18, 26].

The effect of H$_2$ concentration on catalyst activity is shown in Figure 4. Although the object of using H$_2$ is its chain transfer function, but it affect the catalyst activity by increasing it, with addition of H$_2$ to 120 ml/L solvent. However, further increase in H$_2$ concentration, decreased productivity of the catalyst. H$_2$ was added at 40°C, so the concentration of both monomer and H$_2$ were high enough in the solvent.

Influence of increasing monomer pressure from 1 atm to 5 atm was studied which is showed in Figure 5. Productivity of the catalyst increases with increasing monomer pressure up to 2 atm. Higher pressure of monomer at 3 atm decreases activity of the polymer. The activity of the catalyst remains almost constant with monomer pressure higher than 3 atm. Increasing pressure of monomer higher than 2 atm, significantly increases the catalyst activity at the begining, and as the reaction is exothermic, it could deactivate some of the active sites of the catalyst. As a result, the increasing

Table 1. The influence of the MAO concentrations on polymerization behaviour.

MAO(mmol Al)	[Al]/[Zr]	gPE	Rp gPE/mmolZr.h	$\overline{M}_v$	m.p$^{\circ}$C
3	385	9.70	1244	284000	133
4.5	577	18.74	2403	259000	134
6	770	22.60	2897	248000	130.44
7.5	962	22.82	2926	138000	132.11
9	1152	22.22	2845	126000	117.81

(P$_{Ethylene}$) = 2 atm, (polymerization time) = 1 h, [Zr] = 0.0156 mmol/L solvent, (solvent) = 500 mL toluene, (temperature) = 50°C, (stirrer speed) = 800 rpm.

Table 2. The influence of temperature on polymerization behaviour.

Temp(°C)	gPE	Rp gPE/mmolZr.h	$\overline{M}_V$	m.p°C
40	19.72	2528	300000	138
50	22.69	2897	248000	130.44
60	44.92	5759	237000	-
70	38.26	4905	70000	134
80	41.54	5326	51000	134

(P$_{Ethylene}$) = 2 atm, (polymerization time) = 1 h, [Zr] = 0.0156 mmol/L solvent, (solvent) = 500 mL toluene, (temperature) = 50°C, ([Al]/[Zr]) = 770/1, (stirrer speed) = 800 rpm.

Table 3. Comparison of polymerization activity of manufactured catalyst and commercial catalyst.

catalyst Cp₂ZrCl₂	gPE	Rp gPE/mmolZr.h	Monomer pressure (atm)
Manufactured	19.72	2528	2
	19.13	2474	3
Commercial(Fluka)	17.34	2223	2
14693	17.03	2183	3

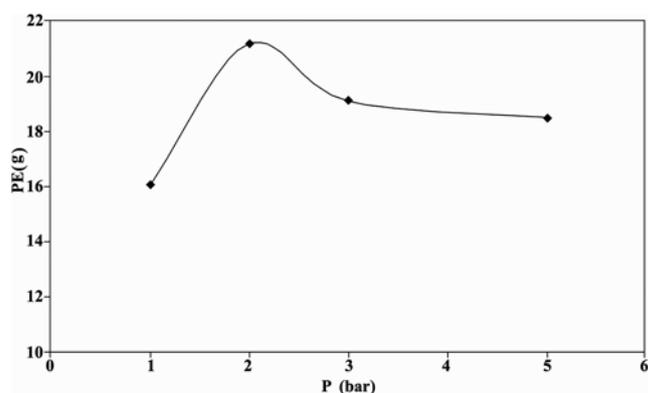(temperature) = 40°C, (polymerization time) = 1 h, [Zr] = 0.0156 mmol/L solvent, ([Al]/ [Zr]) = 770/1.

temperature could destroy structure of the catalyst particulary at the Cp-Zr bond [18, 26].

Comparison of polymerization activity of manufactured Cp₂ZrCl₂ catalyst and the commercial one purchased from Fluka. shows similar polymerization activity (Table 3).
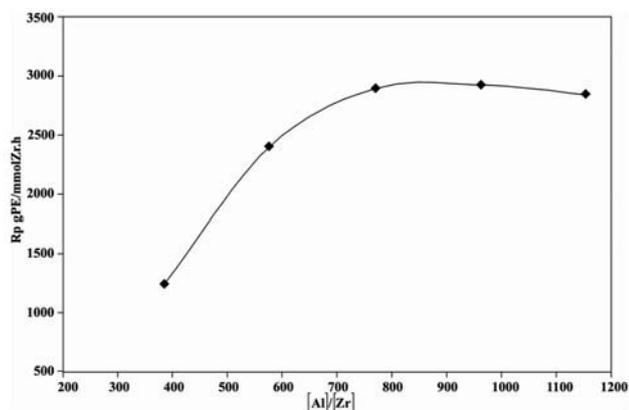
Figure 3. DMTA of polymer obtained at 40°C and monomer pressure = 2 atm.
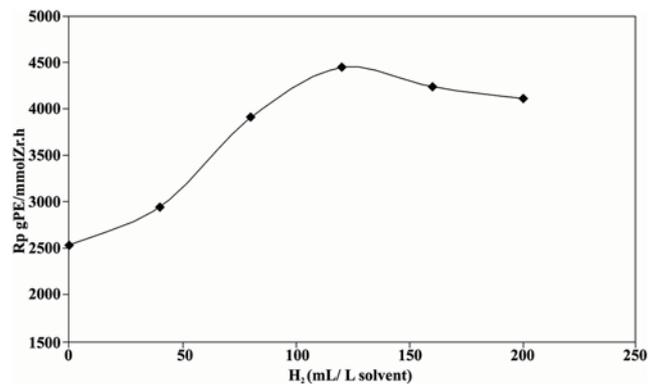
Figure 4. Plot of average rate of polymerization versus H₂ concentration. (temperature) = 40°C, (polymerization time) = 1 h, [Zr] = 0.0156 mmol/L solvent, ([Al]/[Zr]) = 770/1.

Polyethylene Characterization

Some characteristics of polyethylene which was obtained with the Cp₂ZrCl₂/MAO catalyst system get at different polymerization conditions are listed in Table 1 and 2. These results indicate certain conclusions. When the [Al]/[Zr] ratio increases, the $\overline{M}_V$ and the melting point of the polymer decrease (Figure 6 and Table 1). Also, chain transfer is facilitated due to increase of methylaluminoxane concentration [2]. As expected, the increasing hydrogen concentration and temperature also decrease $\overline{M}_V$ (Figure 7 and Table 2). Addition of H₂ dramatically decreased $\overline{M}_V$ of the polymer. Addition of H₂, increasing temperature and, then H₂ facilitates chain transfer which causes reduction of $\overline{M}_V$ [20, 21]. Density of some of the polymer measured

Figure 5. Plot of gPE obtained versus monomer pressure. (temperature) = 40°C, (polymerization time) = 20 min, [Zr] = 0.0156 mmol/L solvent, (solvent) = 500 mL toluene, (temperature) = 50°C, ([Al]/[Zr]) = 770/1 molar ratio, (stirrer speed) = 800 rpm.
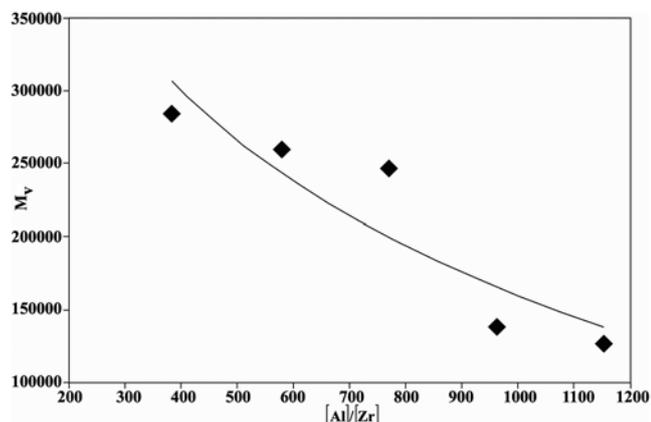
Figure 6. Effect of [Al]/[Zr] ratio on $\overline{M}_v$ of polymer. Polymerization conditions are as detailed in Table1.
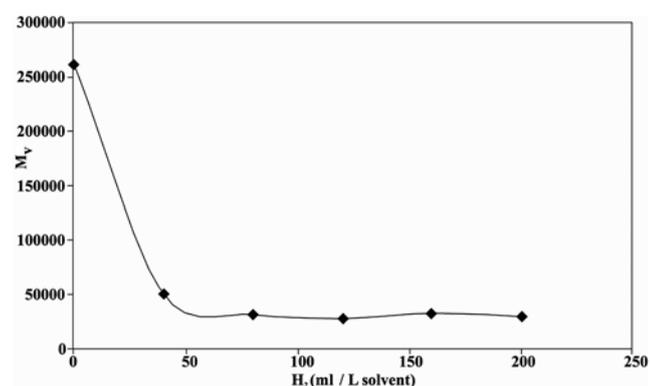

Figure 7. Effect of H_2 concentration on $\overline{M}_v$. Polymerization conditions are as Figure 4.

which was 0.940-0.956 g/cm^3 which is the indication of high density polyethylene.

CONCLUSION

The concluding remarks are as follows:

1. The prepared catalyst was quietly an active catalyst, its activity was comparable with the commercial one.

2. Increasing [Al]/[Zr] ratio increases polymerization activity of the catalyst.

3. Maximum activity of the catalyst was obtained at 60ºC.

4. Addition of H_2 up to 120 cm^3/L solvent increases the activity of the catalyst, while higher concentration of H_2 decreased its activity.

5. Maximum productivity was obtained at 2 atm of monomer pressure.

6. Increasing temperature, [Al]/[Zr] ratio, and H_2 concentration decreased the $\overline{M}_v$ of the obtained polymer.

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