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New strategy to increase comonomer incorporation in LLDPE synthesis using Ziegler-Natta catalysts

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Abstract

Effect of $FeCl_3$ and $FeCl_3/SiCl_4$-doping on the performance of $MgCl_2$ (ethoxide type)/$TiCl_4$/TEAL catalytic system was evaluated in the linear low density polyethylene (LLDPE) synthesis using 1-hexene as the comonomer. Results revealed that $FeCl_3/SiCl_4$ modified catalytic system has better performance in terms of catalyst activity and comonomer incorporation when compared with unmodified catalyst or the catalytic system in the presence of $FeCl_3$ alone. In fact, the introduction of $FeCl_3$ doper, in its optimum amount of 10 wt. %, together with $SiCl_4$induced better catalytic performance with 212 and 90 % increase in catalyst activity and 1-hexene incorporation, respectively.Copolymers characterization showed increased bulk density together with decreased crystallinity and T_m in the polymers from modified catalysts. Overall results showed that, new catalytic system represented in this work, is a good candidate for large scale LLDPE production with high comonomer amount.

Keywords: LLDPE; modified support; $FeCl_3$; Ziegler-Natta catalyst.

Introduction

Ethylene copolymers are an important class of industrial materials.The properties and processing characteristics of these copolymers are through outsubordinate on the amount and distribution of the comonomers.In light of the vast array of different catalyst combinations for this issue, our understanding of the influences of the modifiers on copolymerization characteristic is still evolving.In the last two decades among the polyethylene family(HDPE, LDPE, and LLDPE), LLDPE had the highest production growth rate[1].LLDPE copolymers are manufactured by the copolymerization of ethylene with higher α-olefin monomer like 1-butene, 4-methyl-1-pentene, and 1-hexene. It is generally known that, α-olefin exists in small amount in the copolymer, leads to short chain branches on the polymer backbone[2]. Most of the LLDPE properties can be affected by these short chain branching.

It is accepted that, a wide range properties of LLDPEs can be resulted by altering the number and distribution of short chain branches. In addition, the length of the short chain branch may also play an important role in governing the mechanical properties of the prepared LLDPE[3, 4].

More than 80 % of LLDPE productions are performed by Ziegler-Natta (ZN) catalysts. In fact, heterogeneous ZN catalyst assisted olefin polymerization, is amongst the most important polymerization reactions [5-7]. Therefore, this catalyst plays a prominent role in LLDPE synthesis due to its low cost, accessibility and high performance [8-11].

Three key ingredients containing i) support ii) $TiCl_4$ embedded on the support surface, and iii) an Al-alkyl cocatalyst compose industrial ZN system. $MgCl_2$and Mg (OEt) $_2$ are preferred supports in this case since Mg and Ti have similar atomic radii. Although, $Mg(OEt)_2$ precursor is mainly converted to related $MgCl_2$ during titanation step, ZN catalysts prepared from $Mg(OEt)_2$ precursor received a lot of attention among studied supports due to higher overall catalytic activity [12].As a result, many industrial HDPE and LLDPE plants employ $MgCl_2$ (ethoxide type)/$TiCl_4$ as the active catalyst precursor.

One of the disadvantages in heterogeneous ZNcatalytic system is its low efficiency toward higher α-olefins which lead to low comonomer incorporation in ethylene/α-olefin copolymers. Although many reports describe the preparation of highly active ZN catalyst in ethylene/α-olefin copolymerization [8], however a catalyst with optimal activity and selectivity toward higher α-olefins has not been achieved yet and many concepts are still under discussion.

It was accepted that metal halide derivatives, which can be added to $Mg(OEt)_2$or $MgCl_2$supports, have the ability to change surface properties of them, resulting in the modification of active center distribution of catalysts[13]. Their addition to catalyst systems consequently lead to the improvement in catalytic performance (i.e. catalyst activity and comonomer incorporation) and polymer properties [14-17].

In this study the performance of the $MgCl_2$ (ethoxide type)/$TiCl_4$catalyst in the presence of $FeCl_3$ dopant and $SiCl_4$ modifier is concerned in slurry phase LLDPE synthesis. Activity results of the represented modifier furnishes this catalytic system as a good candidate for large scale LLDPE production with increased polymer yield and high comonomer content.

Experimental

Materials

$Mg(OEt)_2$, $SiCl_4$, $FeCl_3$, THF, and $TiCl_4$ (99 %) were purchased from Merck (Darmstadt, Germany). Ethylene gas in polymerization grade was obtained from Arak Petrochemical Co. (Arak, Iran) and was further purified and dried by passing through purification unit containing molecular sieve filled columns. Toluene and n-hexane were kindly donated by Bandar Imam Petrochemical Co. (Mahshahr, Iran). Triethylaluminum (TEA) cocatalyst and 1-hexene comonomer were purchased from Sigma-Aldrich Chemical Co. (St. Loius, MO, USA). Nitrogen gas with 99.99 % purity was provided from Roham Co. (Tehran, Iran).

Catalyst synthesis

Preparation of the catalysts was carried out according to our previous work[18].A typical procedure is as follows:

First, doped supports were prepared by blending appropriate amounts of $Mg(OEt)_2$ and $FeCl_3$ in THF by vigorous stirring of the mixture at 63 °C and at N_2 atmosphere. After 8 h, the prepared support was separated from the solvent and dried under inert atmosphere at60 °C within 3 hour.

To synthesize the catalysts, 2.0 g of the support was added in to a 250 mL two-necked glass reactor containing 50 mL of toluene under N_2 atmosphere at 50 °C. After 30 min stirring, the temperature was gradually raised to 80 °C. Then, 8 mL $TiCl_4$ was added drop wise to the solution. After 4 h, the supernatant was removed, and thesolid residue was washed twice with 100 mL of toluene and 4 times with 100 mL of dry hexane to remove unreacted $TiCl_4$. The final catalyst was subsequently dried under a flow of hot N_2during 2 h.The characteristic and abbreviation of the synthesized catalysts is summarized in Table1.

Table 1. Labels, abbreviations, and composition of the synthesized catalysts.

Catalyst name	$SiCl_4$*	$Mg(OEt)_2/FeCl_3$ w/w ratio	Ti (wt%)
F_0	NO	100/0	7.78
F_5	NO	5/95	6.40
F_{10}	NO	10/90	4.69
F_{15}	NO	15/85	3.81
F_5-Si	YES	5/95	5.98
F_{10}-Si	YES	10/90	4.41
F_{15}-Si	YES	15/85	3.12

*$SiCl_4$ was added during catalyst synthesis before the addition of $TiCl_4$

Copolymerization procedure

Ethylene/1-hexene copolymerization was carried out in a 1-L Buchi stainless steel reactor (Buchibmd 300, Switzerland) equipped with an anchor type mechanical stirrer. The reactor was charged with 500 mL hexane, 0.15 mol of 1-hexeneand appropriate amount of TEAL to reach Al/Ti=180. After 5 min stirring at 83 °C,10 mg of the synthesized catalyst was added to the reactor and then ethylene gas was fed to induce a reactor pressure of 5 bars.After 1 h stirring, the reaction was stopped, and the product was evacuated and dried under vacuum in80 °C.

Measurements

Comonomer content was measured according to ASTM D 2238 –68 standard test method. This method is based on the side chain methyl groups absorbance of polymer at 1376 cm^{-1}[19]. A Nicolet IS5 FT-IR (USA) instrument was used for the determination of methyl group absorbance in polyethylene chain.Morphology of the synthesized catalysts was observed with a VEGA SEM instrument (TESCAN, Czech Republic).The DSC tests were performed on a DSC Mettler Toledo (Switzerland), under nitrogen atmosphere at a heating rate of 10 °C/min. Degree of crystallinity (X_c) and melting temperature (T_m) were obtained from the second heating scan. X_c was calculated according to the following equation:

$$X_C = \frac{\Delta H_m}{\Delta H_m^+}$$

Where, ΔH_m^+ is the specific melting enthalpy of 100 % crystalline PE (288 J/g) [18]and $\Delta H_m$is specific enthalpy of melting of the sample.

Results and discussion

$FeCl_3$doped $Mg(OEt)_2/TiCl_4$ ZN catalysts, which was just reported in our previous papers[13, 18], had a simple preparation procedure and showed high activity in ethylene homopolymerization. Here we discuss the effect of $FeCl_3$ doping on catalyst activity and comonomer incorporation in ethylene/1-hexene copolymerization. In this regard, Mg $(OEt)_2/FeCl_3/TiCl_4$ catalysts containing 0, 5, 10 and 15 w/w % of $FeCl_3$ in the support structure were synthesized in the presence as well as absence of $SiCl_4$. Catalysts compositions and the abbreviations has been shown in Table 1.

According to the activity results ofFigure1, by increasing $FeCl_3$ amount up to 10 %, activity increased from 185 kg Polym/g Ti·hin undoped catalyst (F_0) to 241 and 368 kg Polym/g Ti·hin F_5 and F_{10}, respectively. Thereafter, by further increase in the $FeCl_3$ amount, a drastic drop in the catalyst activity (-22 %) was observed for F_{15} catalyst. In Fe-Si doping cases, activity increased from 185 kg Polym/g Ti·hin F_0catalyst to 277 kg Polym/g Ti·h in F_5-Si and then reached its maximum amount of 577 kg Polym/g Ti·hin F_{10}-Si, while by further increase in Fe amount to 15 %, catalyst activity dropped as an order of 60 %.

The mechanism of halogen containing modifiers promotion effect in ZN catalysts is still evolving. However, as it had already been shown, $SiCl_4$ on the catalyst structure can act as a promoter and cause an increase in the catalyst activity [9, 13, 20].

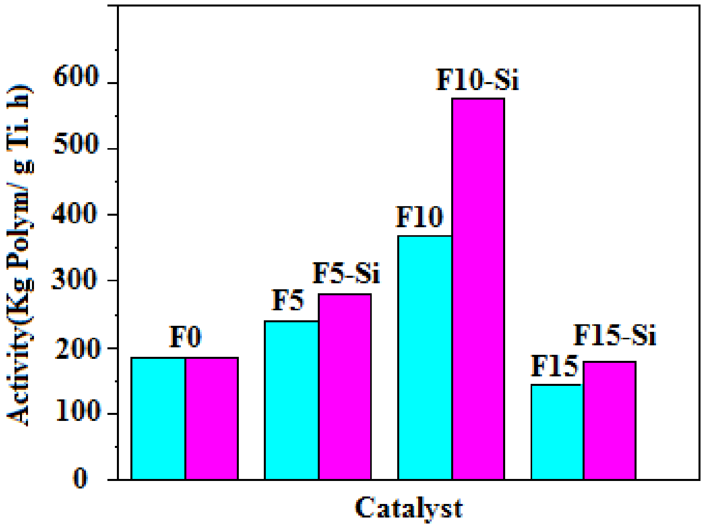

Figure1. Calculated activities for ethylene/1-hexene copolymerization using synthesized catalysts

Comonomer content characterization of the samples has been carried out using FT-IR spectra (Figure 2). In these spectra, the observed bands at 2957, 2920 and 2851 cm^{-1}related to the C-H stretching vibrations of CH_3, CH_2 and CH groups, 1630 and 720 cm^{-1} to the C=C stretching and bending,1468 and 1376 $cm^{-1}$to the deformation of CH_2 and CH_3 groups, respectively[21]. Comonomer content analysis of the synthesized copolymers was summarized in Figure3.Obtained results emphasized that, modification of the catalyst with $FeCl_3$ and combined $FeCl_3/SiCl_4$ lead to dramatic increase (from 2.8 % in F_0 to 4.2 and 5.4 % in F_{10} and F_{10}-Si catalysts, respectively) in the comonomer incorporation.In crescent of comonomer content with modification of the catalyst with $FeCl_3$ and combined $FeCl_3/SiCl_4$ may be due to several reasons as the following:

a) $FeCl_3$ is a stronger Lewis acid in comparison to $MgCl_2$, so the presence of $FeCl_3$ in the catalyst can decrease the density of electrons in active centers and make suitable active centers toward 1-hexeneinsertion[13].

b) the presence of $FeCl_3$ in the catalyst leads to a change in type and distribution of active centers on its surface and in consequence, it constitutes active centers with high capability for copolymerization[22].

c) the presence of $FeCl_3$ in the catalyst leads to diminishing of mechanical properties of the catalyst by the appearance of some cracks in the catalyst surface (see Figure 4), so the disintegration of the catalyst particles occurs easier. This lead to higher catalyst activity in doped supports.

Morphologies of catalysts obtained from scanning electron microscopy (SEM) were shown in Figure 4. As it is obvious from that Figure, all of catalysts showed almost spherical morphology. Detailed examination of the pictures revealed that with the addition of $FeCl_3$, narrow cracks appeared at the catalysts surface (Figure 4-b and 4-c). These cracks made catalyst fracture easier and lead to higher catalytic activity.

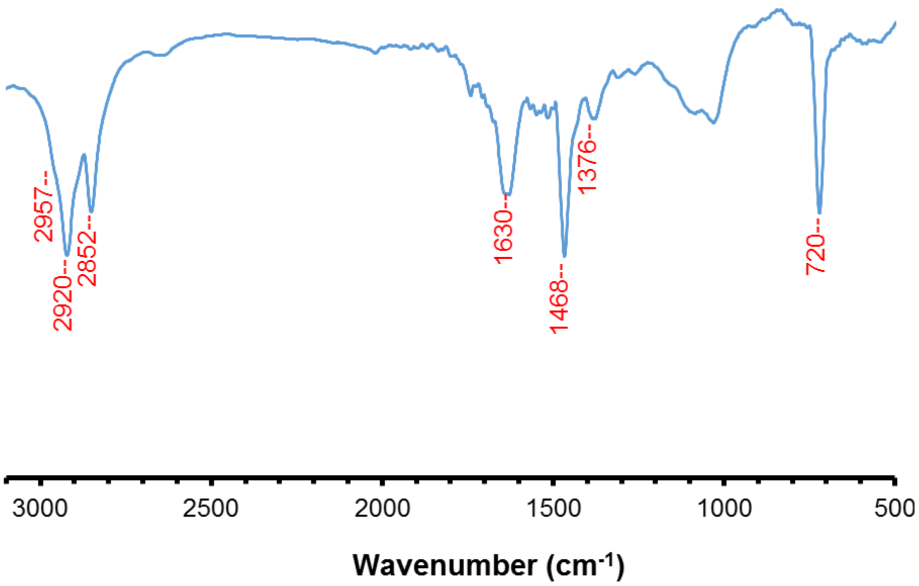

Figure 2. FT-IR spectrum of the synthesized copolymer with F_5 catalysts as an example.

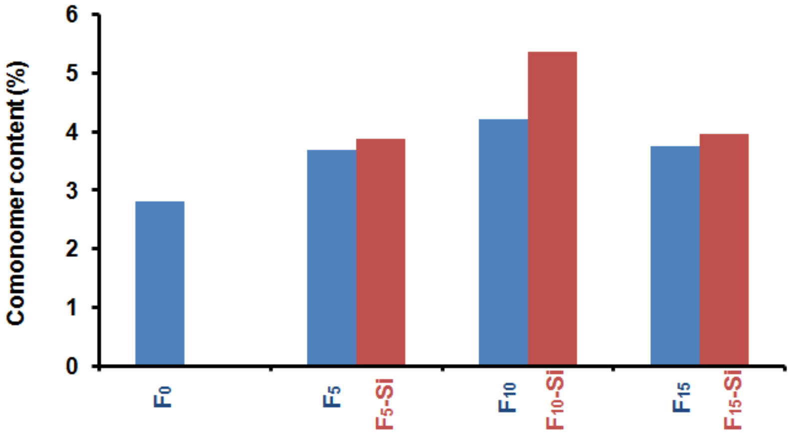

Figure 3. Comonomer incorporation abilities of the synthesized catalysts in ethylene/1-hexene copolymerization

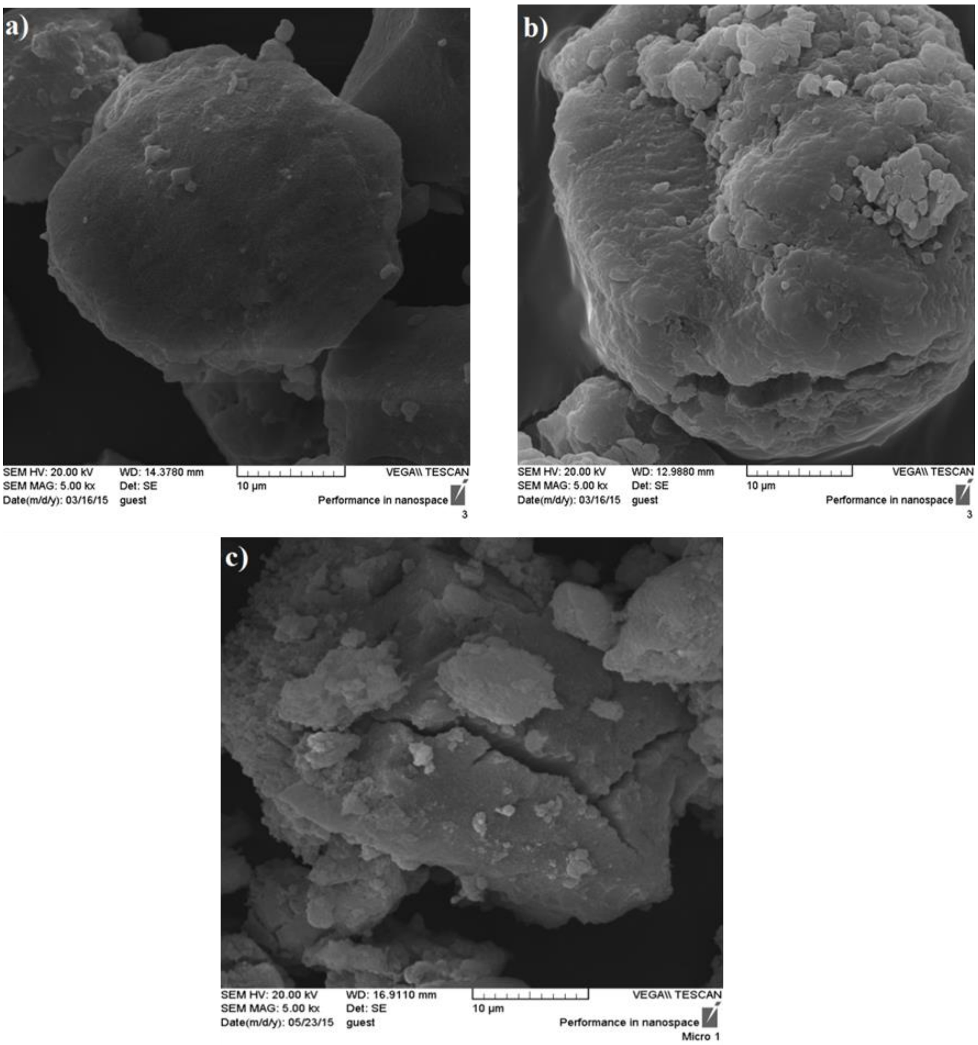

Figure 4. SEM images of synthesized catalysts: a) F_0, b) F_{10}; and c) F_{15}

In order to investigate crystallinity and thermal properties of the produced copolymers with different catalysts, differential scanning calorimetry(DSC) was conducted at a heating rate of 10 °C/min [23-25].Obtained curves were shown in Figure5 and the results were collected in Table 2. According to the data of Table 2, produced copolymers by catalysts containing 5 and 10 % $FeCl_3$ and combined $FeCl_3/SiCl_4$ had less melting temperature and crystallinity percentage in comparison to the unmodified catalyst (F_0), so that, the melting temperature and crystallinity percentage of the produced copolymers decreased from 131.6 °C and 53 % in unmodified catalyst to a range of 128.7-130.4 °C and 44-47 % in the modified catalysts, respectively (Figure5). This decrease in X_c and $T_m$is an evidence of increased comonomer amount in the backbone of the copolymers [26-29].

On the other hand, T_m and X_c of the produced polymers via F15 and F15-Si catalysts increased again. The advent of such effect is unclear to us and needs further consideration.

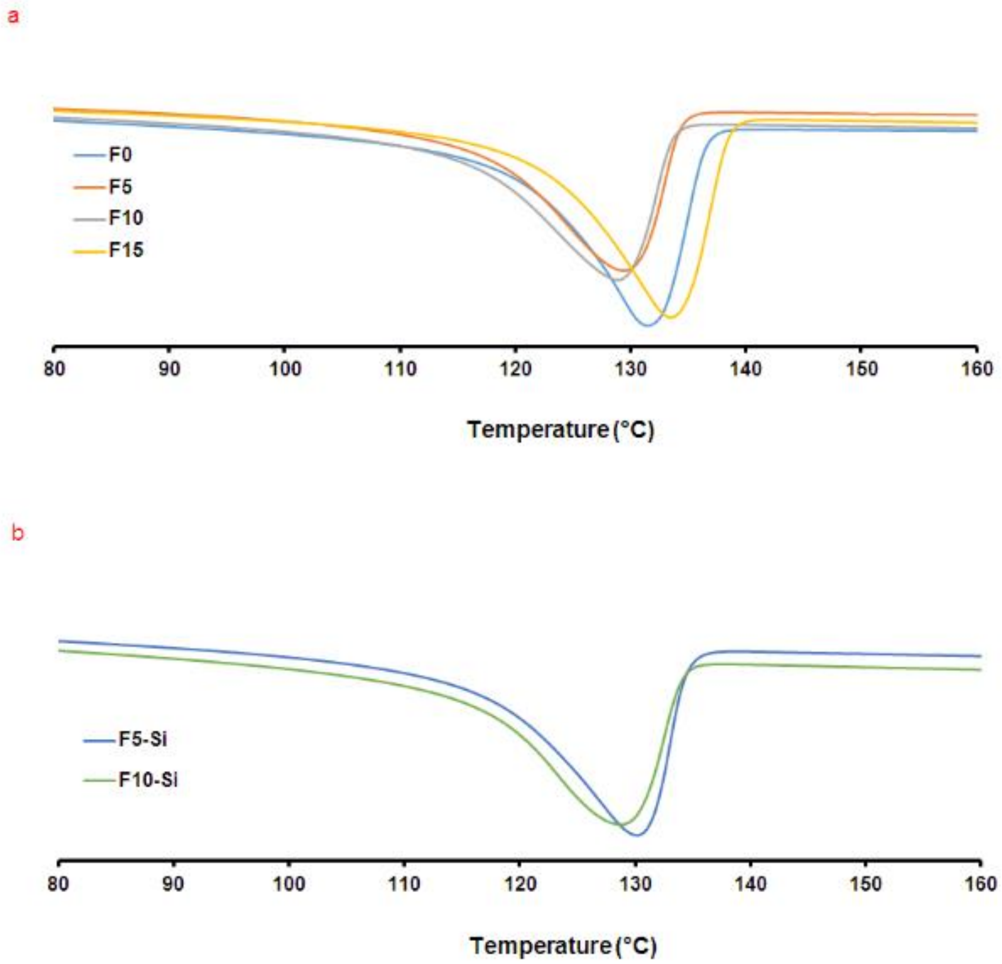

Figure5. DSC curves of prepared samples with a) $FeCl_3$-doped, and b) $FeCl_3/SiCl_4$-doped catalysts

Table 2. Results of DSC, and bulk density characterization of ethylene\1-hexene copolymers produced via different catalyst systems.

Catalyst code	F_0	F_5	F_{10}	F_{15}	F_5-Si	F_{10}-Si	F_{15}-Si
Crystallinity (%)	53	47	46	53	45	44	53
T_m (°C)	131.6	130.4	129.0	133.4	130.4	128.7	132.0
Bulk density (gr/ml)	0.22	0.34	0.37	0.30	0.34	0.37	0.31

The bulk density of produced copolymers increased drastically from 0.22 g/mL to a range of 0.30-0.37 g/ml in the produced copolymers with modified catalysts (see Table2). The increase in the bulk density of produced copolymers with doped catalysts can be attributed to the presence of $FeCl_3$ in the catalyst which caused catalyst breakage to occur easier in the polymerization pool, subsequently a smaller copolymer particle size was produced which raised bulk density.

Conclusions

Linear low density polyethylene (LLDPE) as synthesized by a series of $FeCl_3$ and $FeCl_3$/$SiCl_4$modified $MgCl_2$ (ethoxide type)/$TiCl_4$ catalytic system using 1-hexene as comonomer.Obtained copolymers were characterized in terms of their comonomer content, catalyst activity, bulk density, crystallinity, and melting point.The catalyst activity profile showed that in the presence of suitable amount of $FeCl_3$,catalyst activity increases, whereas decrease of the catalyst activity was observed in higher $FeCl_3$ content. DSC analysis demonstrated that the melting temperature and crystallinity percentage of the produced copolymers were decreased compared to obtained copolymer from pristine catalyst.With doping of $FeCl_3$ /$SiCl_4$ to the catalytic system, comonomer content and bulk density of the copolymers increased as well. Our results suggested new/modified catalytic system which has better performance in terms of catalyst activity and comonomer incorporation than old/conventional ZN catalyst based on $TiCl_4$/$MgCl_2$in LLDPE synthesis.

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