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Polyolefins Journal, Vol. 4, No. 2 (2017)
DOI: 10.22063/poj.2017.1467

ORIGINAL PAPER

Effects of $FeCl_3$ doping on the performance of $MgCl_2$/$TiCl_4$/DNPB catalyst in 1-hexene polymerization

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Received: 10 March 2017, Accepted: 17 May 2017

ABSTRACT

The aim of this study was to examine the effect of catalyst doping on the performance of $MgCl_2$. EtOH/$TiCl_4$ catalyst system. In this regard, a series of undoped as well as $FeCl_3$-doped catalysts was prepared and employed in 1-hexene polymerization. A modified catalyst containing 10 wt. % of $FeCl_3$ dopant demonstrated the highest activity, with 32% activity increase compared to unmodified one, among the series. The GPC results showed a lower molecular weight as well as broader MWD for the poly1-hexenes obtained from $FeCl_3$-doped catalyst. The distribution of active centers was analyzed using deconvolution of the MW profiles with using multiple Flory functions. It was demonstrated that the number of active sites increased by 10 wt. % $FeCl_3$ doping, however, by more increasing the dopant amount to 15 wt.%, the number of active sites decreased. The ^{13}C-NMR results indicated that, $FeCl_3$ doping did not have a considerable effect on the polymer tacticity (with total tacticity of 53 %), however it increased by donor presence to the maximum value of 60 %. **Polyolefins J (2017) 4: 253-262**

Keywords: Ziegler-Natta catalysts; 1-hexene polymerization; poly(α-olefin); tacticity.

INTRODUCTION

Higher poly(α-olefins) based polymeric materials such as poly1-hexene and poly1-octene have a wide range of applications including lubricating oil composition, adhesive, valve seal and also as one of the components of cosmetically suitable carrier in antiperspirants and deodorants [1-3]. Multi sites Ziegler-Natta (ZN) catalyst systems not only provide the opportunity for developing high yield process but also are capable of tailoring the critical characteristics of poly(α-olefins) such as stereoregularity and molecular weight characteristics [4, 5]. The interest in polyolefins synthesis using high performance ZN systems led to study the relationship of catalyst system, polymerization performance and product characteristics [6-10]. There have been various studies regarding to the kinetics of polymerization, molecular weight, molecular weight distribu-

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tion and tacticity of the polymers in literature. Dandge et al. [11] studied the kinetics of 1-hexene polymerization by employing a $TiCl_3$-$AlEt_3$ catalyst system. Kothandaraman [12] studied the kinetics of 1-octene polymerization using $MgCl_2$-supported $TiCl_4$ along with triethyl aluminum as cocatalyst. The two major targets of the studies on the α-olefin polymerization include the control of the molecular weight (MW) and molecular weight distribution (MWD) of polyolefin and also control of its tacticity. Most of the properties of polyolefins, such as physical-mechanical properties and processability, are severely influenced by the molecular weight distribution and tacticity of the materials. It has been realized that the MWD of polyolefin is determined by the distribution of active centers (ACD) in the catalyst, which is a function of the surface structure of the $MgCl_2$ support [13]. Moreover, the ACD of the supported catalyst is influenced dramatically by the surface structure of $MgCl_2$ [14, 15]. Therefore, controlling of polyolefins properties can be realized by modification of $MgCl_2$ support. Kissin et al. [16] described chemical reactions between a $TiCl_4/MgCl_2$/diisobutyl phthalate-type ZN catalyst and $AlEt_3$-(Cy)(Me)$Si(OMe)_2$ and concluded that all of the adsorption and reactions occurred on the surface of $MgCl_2$. Thus, the modification of the surface structure of $MgCl_2$-supported ZN catalysts is very important in controlling the MWD and isotacticity of polyolefins. Nevertheless, there were only few reports in this field. An effective way of modification of the surface structure of supported ZN catalysts is doping a certain amount of inorganic compounds in the supports. ZN catalysts based on $MgCl_2$ doped with manganese (Mn) and zinc (Zn) halides were prepared by Garoff and Leinonen [17] and Fregonese and Bresadola [18], respectively, and ZN catalyst based on $Mg(OEt)_2$ doped with (Fe) was prepared by Bazvand et. al. [19]. The latter group was concluded that $FeCl_3$ doping had considerable effect on the performance of $Mg(OEt)_2$-based ZN catalyst toward catalyst activity and polymer properties, while that the level of such effect in $MgCl_2$-based catalysts is still remained unknown.

In order to improve the stereoselectivity of $MgCl_2$-supported titanium catalysts, different types of electron donors have been introduced into them [20]. In doing so, the internal donor (ID) is believed to coordinate preferentially to (110) cut of $MgCl_2$, selectively poison poorly stereoselective active sites, or transform certain types of a specific sites into highly stereospecific ones [21]. However, there are still no enough experimental data on the changes of active center distribution made by the internal donors. Therefore, a detailed investigation into these changes may be the best way to develop the knowledge on the effects of internal donor.

In this work, first $FeCl_3/MgCl_2$•EtOH adducts with different $FeCl_3$ contents of 10 and 15 w/w % were prepared via the co-precipitation method. Then, they were employed in the synthesis of a series of $FeCl_3/MgCl_2/ID/TiCl_4$-type ZN catalysts which were subsequently used in 1-hexene polymerization. The effect of $FeCl_3$ dopant on the isotacticity, thermal behavior and MWD of poly1-hexenes (PHs) was investigated.

EXPERIMENTAL

Materials

$FeCl_3$, $MgCl_2$, THF, toluene, n-hexane and $TiCl_4$ (99%), di-n-butyl phthalate (DNBP), triethylaluminum (TEA), and 1-hexene were purchased either from Merck (Darmstadt, Germany) or Aldrich Chemical Co. (Munich, Germany). Toluene and 1-hexene were dried by distilling over benzophenone/sodium under N_2 atmosphere prior to use. Nitrogen gas with 99.99 % purity was supplied from Roham Co. (Tehran, Iran).

Preparation of $MgCl_2$•EtOH adduct

Spherical $MgCl_2$ adduct was prepared according to a method that was published by our group, previously [22]. A typical procedure is as follows: dried $MgCl_2$ powder and $FeCl_3$ (10 and 15% w/w) were placed in a two jacket stainless steel reactor under dry N_2 atmosphere. A calculated amount of absolute EtOH [(EtOH)/($MgCl_2$)=3.3] was also added into the reactor. The mixture was mixed and the whole was heated to 50°C. At this stage, silicon oil (200 mL) was added and the mixture temperature was raised to 120°C. After 6 h, the suspension transferred to another jacket vessel containing n-heptane (500 mL) at -30°C and held at this temperature for 1 h under stirring. By decanting, a solid product was collected in a nitrogen atmosphere. The solid was repeatedly washed with n-heptane to remove paraffin oil, filtered, and dried at room temperature in vacuum. The supports composition is shown in Table 1.

Preparation of catalysts

Preparation of the catalysts was done according to a method that was published by Rahbar et. al. [23, 24]. To prepare the catalyst, 20 mL of $TiCl_4$ was added dropwise on the solution of 2 g of the support in toluene at -5°C and kept at this temperature for 20 min with continuous stirring. The temperature was gradually raised to 60°C and di-n-butyl phthalate (internal electron donor) was added in this temperature. The system was kept under these conditions for 30 min. Then the temperature of mixture was increased to 90°C and kept at this temperature for 1 h. After the time of first impregnation, the supernatant was removed and the catalytic solid was washed three times with dry toluene followed by the addition of 40 mL of $TiCl_4$. The temperature raised to 110°C and kept at this condition for 1 h, after which the supernatant was removed and the catalytic solid was washed again with dry toluene at 110, 100 and 90°C until no residue of HCl was observed. The catalyst was washed several times with dry heptane at 85°C until no trace of titanium was detected in the washing liquid. The obtained catalyst was dried until constant weight under nitrogen flow.

1-hexene polymerization

A mixture of 0.08 mole of 1-hexene and 50 mL of n-hexane was taken in a three necked round bottom flask and flushed with dry nitrogen. The cocatalysts by a ratio of Al/Ti =30 were injected into the system. Then, 10 mg catalyst under nitrogen gas was added to the system and the polymerization started. The mixture was stirred magnetically for 2 h at 50°C. The reaction was stopped after 2 h and the polymer was precipitated in a tank containing a mixture of 200 mL of ethanol and 1 mL of hydrochloric acid. The resulting product was rinsed and dried in vacuum.

Table 1. Composition and abbreviation of the prepared supports.

Support precursor	$FeCl_3$ amount (Wt. %)	Support code
$MgCl_2 \cdot EtOH$	0	F0
$MgCl_2 \cdot EtOH/FeCl_3$	10	F10
$MgCl_2 \cdot EtOH/FeCl_3$	15	F15

Characterization techniques

XRD (X-ray diffraction) analysis of the supports was obtained on a Siemens D-5000 X-ray diffractometer (USA) operating with a copper target (λ= 1.54 Å) at 25 mA and 40 kV and at a scanning rate of $3°min^{-1}$. The morphology of the supports was observed by scanning electron microscopy (SEM model S-3000 N, Hitachi, Japan) after coating with a gold sputter coating machine (model E-1010, Hitachi, Japan). For determination of Ti content of the catalyst, after sample digestion in H_2SO_4, Ti was oxidized with H_2O_2 and analyzed by UV–visible spectrophotometer (λ= 410 nm) in a Shimadzu 100 spectrophotometer model (6800, USA). The molecular masses and their distributions were determined by gel permeation chromatography (Waters GPCV 150+, USA), using THF as the eluent at room temperature. Glass transition temperature (Tg) of the polymers was captured from the first heating scan of DSC test using DSC Q 1000 of TA (USA) instrument, at a heating rate of 5°C/min under nitrogen atmosphere. The tacticity of polymers was obtained from the ^{13}C-NMR spectra recorded on a Bruker Avance-400 spectrometer in $CDCl_3$ at the frequency of 500 MHz, at 45°C.

RESULTS AND DISCUSSION

Characterization of the supports

Powder X-ray diffraction

XRD pattern of anhydrous $MgCl_2$ and $MgCl_2 \cdot EtOH$ adduct was analyzed elsewhere [22, 24], so here we only focus on the XRD pattern of F10 adduct. It had already been shown that pure $FeCl_3$ could show five peaks at 2θ = 19, 39, 42, 55, 68° [19], while the XRD spectrum of $FeCl_3$-doped $MgCl_2$ showed none of these peaks (Figure 1). The absence of $FeCl_3$ peaks in the XRD pattern of $FeCl_3/MgCl_2$ support confirms that $FeCl_3$ was dissolved in $MgCl_2$ structure and a new $MgCl_2/FeCl_3$ solid solution was formed. In this new structure, Mg was partially replaced by Fe_{II} ions, since their ionic radius are close to each other (Mg_{II} = 0.88

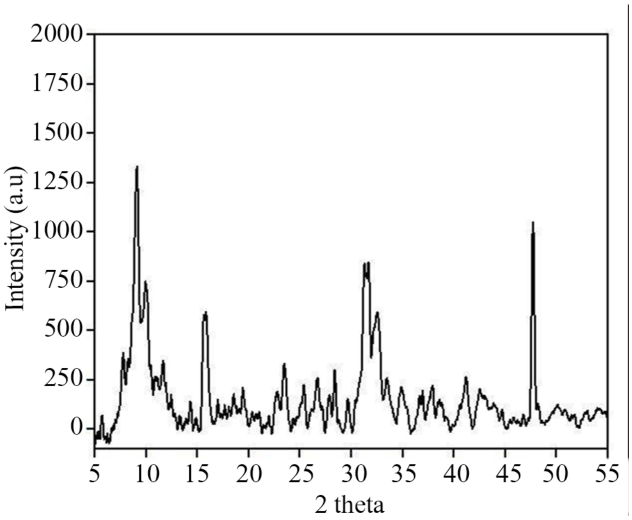


Figure 1. XRD pattern of F10 adduct.

Å, Fe_{II} = 0.84 Å). On the other hand, the main peaks of the XRD pattern of F10 adduct appeared at $2\theta \approx 10°$ (which is usually emerged in activated $MgCl_2$ [25]), at 2θ~16° (due to the stacking of -Cl-Mg-Cl- triple layers along the crystallographic direction), at 2θ=32° (related to the cubic close packing with rhombohedra structure of anhydrous $MgCl_2$ [26]) and at 48° (due to stacking faults in the triple layers [26-28]) confirm the presence of $MgCl_2$ structure.

Surface morphology studies

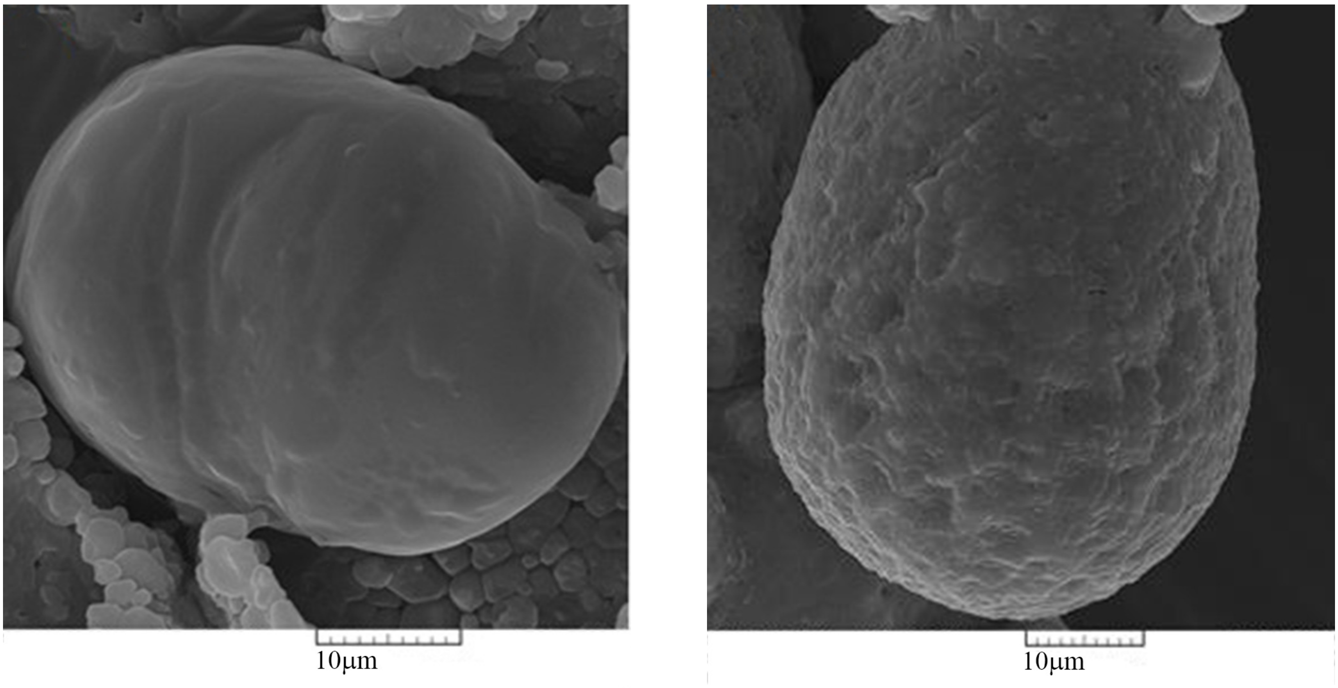
The support morphology has considerable effect on the ZN catalyst performance. Indeed, it replicates the catalyst morphology. In order to study the effect of $FeCl_3$ doping on the support morphology, SEM images were considered. As can be seen in Figure 2, although both adducts have high spherical morphology, F0 shows a smoother surface. Hence, in the presence of $FeCl_3$, adduct loses its smooth surface and the surface becomes uneven.

Characterization of the catalysts

Titanium content

The catalysts composition and Ti content are shown in Table 2. CF0 contains $MgCl_2$·EtOH reacted with $TiCl_4$, CF10 contains $MgCl_2$·EtOH with $FeCl_3$ (10 %) reacted with $TiCl_4$, CF15 contains $MgCl_2$·EtOH with $FeCl_3$ (15 %) reacted with $TiCl_4$ and CF10-D contains $MgCl_2$·EtOH with $FeCl_3$ (10 %) in the presence of DNBP donor reacted with $TiCl_4$.

UV-visible technique was used to achieve titanium content of the catalysts (Table 2). As can be seen, Ti content of the $FeCl_3$-modified catalysts (CF10 and CF15) shows a decrease in comparison with the unmodified one (CF0). According to the results of DFT, an increase in the number of iron atoms in the support structure decreases the binding energy between $TiCl_4$ and the support. In other words, the presence of Fe



(a)

(b)

Figure 2. SEM images of (a) F0 and (b) F15 adducts.

Table 2. Composition, abbreviation and Ti content of the prepared catalysts and their activity in 1-hexene polymerization$^{(a)}$.

	Catalyst Code	Ti %	Activity (g PHs/g Ti· h)
$TiCl_4$/F0	CF0	8.23	11,600
$TiCl_4$/F10	CF10	7.51	15,300
$TiCl_4$/F15	CF15	6.42	13,600
$TiCl_4$/F10/DNBP	CF10-D	5.61	18,400

$^{(a)}$ Polymerization conditions: Cocatalyst: TEA, Al/Ti=30, T=50 °C, t =2h

atoms reduces the tendency of $TiCl_4$ for adsorption on the $MgCl_2$ surfaces [19]. Furthermore, the Ti content decreases by the addition of DNBP on the catalyst, demonstrating a strong interaction between $TiCl_4$ and the internal donor due to the point that $TiCl_4$ can also behave as a Lewis acidic site to the donor molecules [29].

Catalytic activity

The activity results in the 1-hexene polymerization catalyzed by synthesized catalysts are shown in Table 2. It can be seen that the support doping has remarkably increased the catalyst activity from 11600 g PHs/g Ti·h in the undoped catalyst to 15,300 and 13,600 g PHs/g Ti·h in CF10 and CF15, respectively. Indeed, increasing the amount of $FeCl_3$ tends to exhibit higher catalytic activity, as long as the $MgCl_2/FeCl_3$ feed ratio is equal to 90:10. However, catalyst doping with more than 10 % w/w of $FeCl_3$ results in a decrease in activity indicating that the amount of doping agent has an important role in the catalytic performance [18, 19]. In addition, the activity increases as a result of the addition of internal electron donor. In fact, donor adsorbs on the surface of those defects which form less active centers and the remained defective $MgCl_2$ sites became accessible to $TiCl_4$ adsorption in order to form stable active centers with high activity. Ti content on the catalyst and the sum of active sites reduce, however, the number of stable active site increases. So, the addition of DNBP improves the activity of catalyst in 1-hexene polymerization [30].

Characterization of poly1-hexenes

Stereoregularity of poly1-hexenes

^{13}C-NMR is the most powerful method for studying polyolefins microstructure [31-33]. The ^{13}C-NMR patterns of the poly1-hexenes obtained using the catalysts CF10 and CF10-D are shown in Figure 3. In order to understand the configurational arrangement of 1-hexene monomer unit in the PHs obtained by using different catalytic systems, the first methylene carbon in the side chain ($33.5<\delta<35.0$ ppm) was considered as the most sensitive atom toward stereoregularity [31, 32].

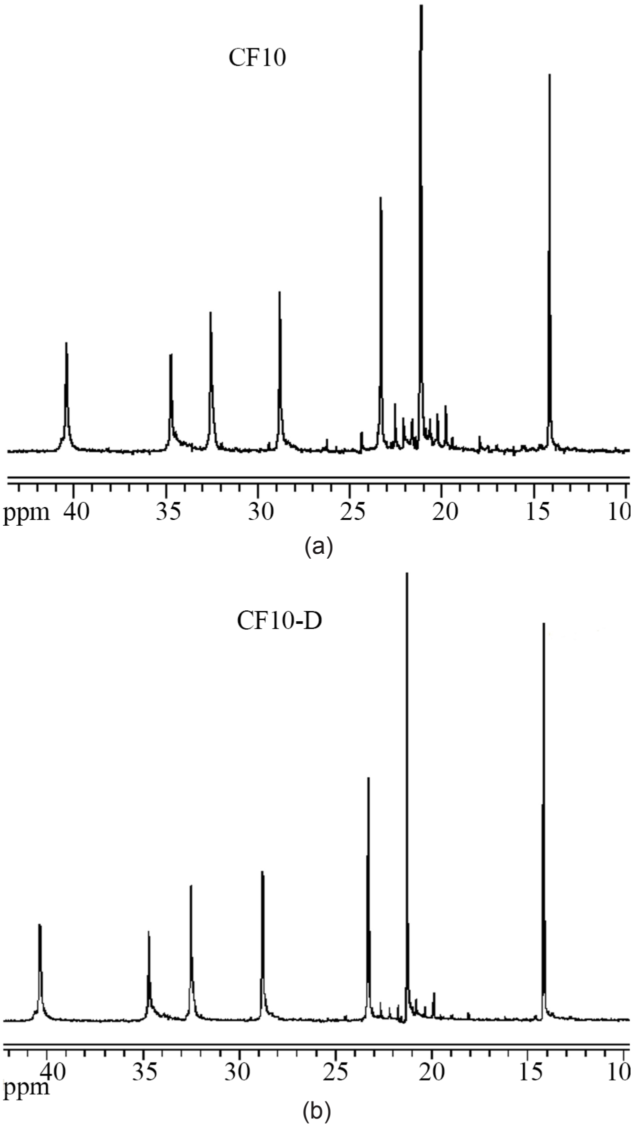


Figure 3. ^{13}C-NMR spectra of poly1-hexenes obtained from the CF10 and CF10-D catalysts.

The peaks located at ~ 34.6-34.8, 34.4-34.6, 34.2-34.4, 34.0-34.2, 33.8-34.0 and 33.6-33.8 ppm, are respectively attributed to the pentad “mmmm”, the “mmmr+rmmr+mmrr”, the “mmrm+rmrr”, the “mrmr+rrrr”, the “mrrr” , and the “mrrm”, respectively [32, 34] (see Figure 4). The degree of isotacticity was calculated as the ratio between the isotactic pentads integral [mmmm] and the sum of all the carbon α-pentads. For the syndiotacticity degree, the

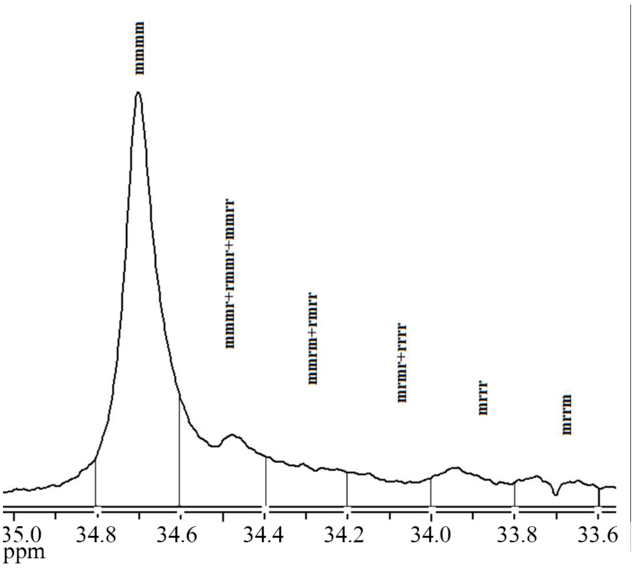


Figure 4. Expanded side chain methylene (C3) resonance pattern of the PH produced by the CF10-D catalyst.

ratio of [rrrr] integral pentads and the sum of all the carbon α-pentads were used as a criterion. Syndiotactic poly(α-olefin), the [rrrr] pentad resonance covered the [mrmr] pentad region; however, the error of taken all this region as [rrrr] pentad should be low as in a syndiotactic poly(α-olefin) the [mrmr] pentad is fairly present [35]. The amount of [mmmm] pentads increased from 54 % in CF0, CF10 and CF15 to 60 % in the catalyst CF10-D (see Table 3). In addition, mmrm+rmrr pentad decreased from 12% in CF0, CF10 and CF15 to 7 % in the catalyst CF10-D, indicating that the DNBP increases isotacticity and reduces the atactic amounts.

MW and MWD of poly1-hexenes

The data shown in Table 4 are molecular weight and molecular weight distribution of PHs obtained with the four catalysts under study.

They clearly show that the M_n and M_w of PH samples decrease from 78,580 and 559,76 g/mol in the undoped catalyst to 43,025 and 400,110 g/mol in the Fe-doped catalyst (CF10), respectively. Although, all the synthesized PHs showed a broad PDI which was expected from a multi-site Ziegler-Natta catalyst. The PH synthesized with CF10 showed a wider PDI among the series. This phenomenon can be explained as the formation of new types of active centers by doping $FeCl_3$ in the $MgCl_2$ support [32, 36, 37]. Furthermore, increasing $FeCl_3$ content (more than 10 %) in the catalyst structure, resulted in a complete deactivation of some active sites [36]. Therefore, the polydispersity of the polymer decreased, while the MW increased. In addition, the MW and MWD were also influenced by the addition of internal donor. Indeed, the addition of the DNBP leads not only to the noticeable increase in isotactic fraction, but also to remarkable change in the molecular weight and narrowing of the molecular weight distribution of PHs probably due to poisoning of some non-specific sites by electron donor [21, 38].

Non-linear fitting of the MWD profiles of poly1-hexene

Deconvolution of polymer MWD curves by multiple Flory functions is known as a helpful way in order to study the distribution of active centers in the catalyst. Each Flory component is believed to be the MWD curve of polymer produced by one family of active centers, with a polydispersity index equals to 2.0. Figure 5 shows the MWD curves of PH samples and their deconvolution into Flory components. The deconvolution results show that five and six types of active centers exist in the undoped catalyst CF0, and 10 % $FeCl_3$-doped catalyst (CF10), respectively. Further increase in the $FeCl_3$ amount resulted in a complete deactivation of some active centers [36], leading to the decrease in the number of Flory components in CF15. Addition of DNBP decreased the number of active centers to five, and indicated that DNBP could deactivate some active sites [21, 39].

Table 3. Tacticity pentad content in C_3 methylene region.

Catalysts	mrrm %	mrrr %	mrmr+rrrr %	mmrm+rmrr %	mmmr+rmmr+mmrr %	mmmm %
CF0	5	6	7	12	16	54
CF10	5	6	7	12	16	54
CF15	5	6	7	13	16	53
CF10-D	5	6	6	7	16	60

Table 4. Molecular weight and its distribution and glass transition temperatures of the PHs prepared by different catalysts(a).

Catalysts	M_w (gr/mol)	M_n (gr/mol)	PDI	T_g (°C)
CF0	559,760	78,580	7.1	-35.03
CF10	400,110	43,025	9.3	-35.03
CF15	484,480	62,669	7.7	-37.05-
CF10-D	420,700	52,308	8.0	-36.52

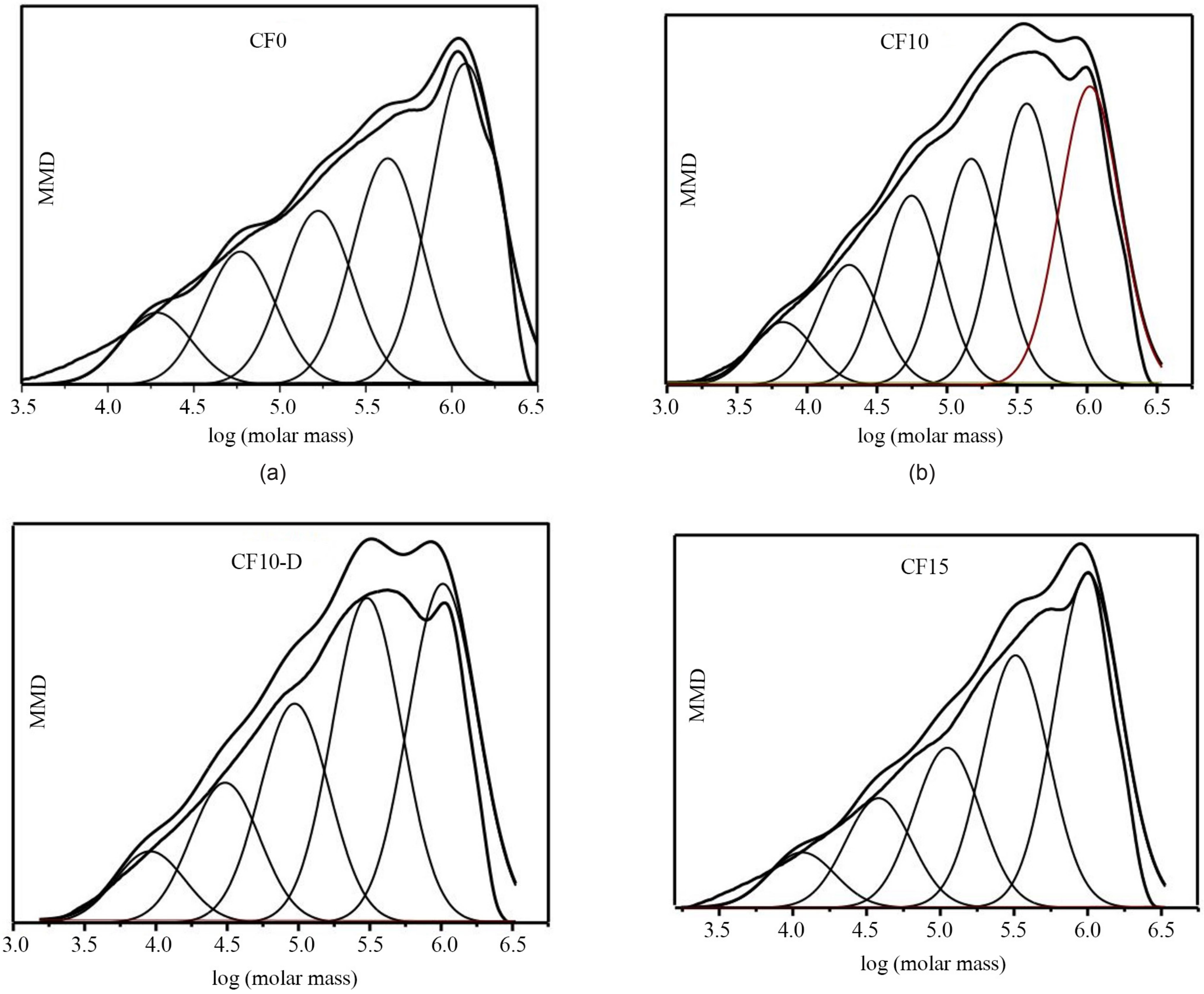
(a) Polymerization conditions: Cocatalyst: TEA, Al/Ti=30, T=50 °C, t =2 h

Thermal properties of the poly1-hexenes

DSC analysis was conducted in a rate of 5°C/min [33, 40-42] to examine the thermal behavior of the PHs. Figure 6 shows the DSC thermograms of the PHs obtained by the four catalysts CF0, CF10, CF15 and CF10-D. All analyzed samples showed only T_g transitions at about -35 to -37°C (see Table 4), although they had different molecular weights. It means that the molecular weights of the obtained PHs were high enough to be neglected. This is in good agreement with the data obtained by other researchers [33, 43]. The absence of T_m in the DSC curves, even in the PH synthesized from the CF10-D system with high isotacticity of 60 %, is an indication of rubbery behavior of the PH samples. It is concluded from this section that neither Fe doping nor DNBP presence could not alter thermal behavior of the PHs.

CONCLUSION

Four catalysts with different $FeCl_3$ content and DNBP



(a)

(b)

(c)

(d)

Figure 5. MWD curve of the PHs synthesized by different catalytic systems.

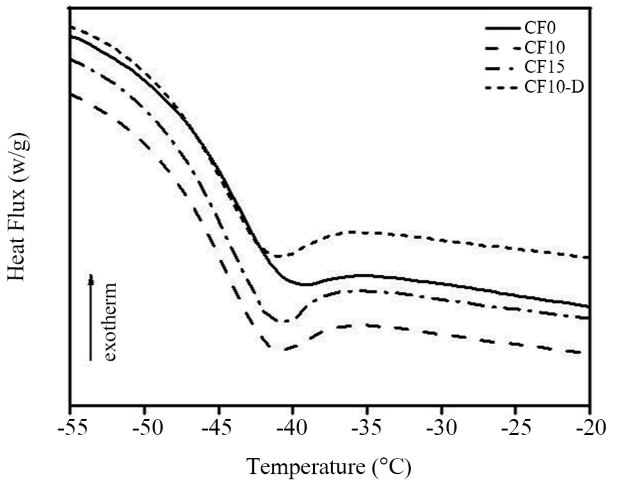


Figure 6. DSC curves of the poly1-hexenes obtained with using different catalysts.

as internal donor were prepared by the reaction of $MgCl_2/FeCl_3$-ethanol adduct with $TiCl_4$. WAXD analysis showed that $FeCl_3/MgCl_2$ solid solution was formed in the doped adducts. The $FeCl_3$-doped catalysts exhibited higher activity in 1-hexene polymerization in comparison with the catalyst supported on pure $MgCl_2$. MWD of PHs broadened with an increase in $FeCl_3$ content of the catalysts. The deconvolution of the MWD curves by multiple Flory functions indicated that the distribution of active centers of $MgCl_2$-supported ZN catalysts could be effectively changed by doping a certain amount of $FeCl_3$ in the $MgCl_2$ support. $FeCl_3$ doping did not alter the isotacticity index of synthesized PHs, while the DNBP increased its amount significantly. Finally, the results of DSC indicated that the T_gs of the samples were in the range of -35 – -36°C.

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