

## Synthesis of high molecular weight polyethylene using FI catalyst

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### ABSTRACT

A FI Zr-based catalyst of bis[*N*-(3,5-dicumylsalicylidene)-2',6'-diisopropylanilinato]zirconium(IV) dichloride was prepared and used for polymerization of ethylene. The effects of reaction conditions on the polymerization were examined in detail. The increase in ethylene pressure and rise in polymerization temperature up to 35°C were favorable for catalyst/MAO to raise the catalytic activity as well as the viscosity-average molecular weight ( $M_v$ ) of polyethylene. The activity of the catalyst was linearly increased with increasing MAO concentration and no optimum activity was observed in the range studied. Although introduction of the bulky cumyl and 2',6'-diisopropyl alkyl substitution groups on *ortho* positions to the phenoxy-oxygen and on phenyl ring on the *N*, respectively enhanced the viscosity average molecular weight ( $M_v$ ) of the obtained polymer strongly, diminished the activity of the catalyst. Neither the activity of the catalyst nor the ( $M_v$ ) of the obtained polymer were sensitive to hydrogen concentration. However, higher amount of hydrogen could slightly increase the activity of the catalyst. The ( $M_v$ ) of polyethylene ranged from  $2.14 \times 10^6$  to  $2.77 \times 10^6$  at the monomer pressure of 3 and 5 bar, respectively which are much higher than those of the reported FI Zr-based catalysts. **Polyolefins J (2014) 1: 25-32**

**Keywords:** FI catalyst, high molecular weight, polyethylene, ethylene polymerization.

### INTRODUCTION

Outstanding scientific and technological developments have made the polyolefin industry one of the most successful growing industries in the area of large volume materials. Development of new catalysts with transition metals has played a substantial role in the fast-growing polyolefins industry. Improvement of new, better performing, less costly polyolefins has often been the result of catalyst development.

However, polymerization processes of olefins, beside the requirement of highly active catalyst to control the particle size, particle size distribution, and morphology of the resultant polyolefin powder are quite important [1]. In the past decade, there have been many rapid advances made in the catalysis of olefin polymerization by non-metallocene complexes, including the early and late transition metals [2]. Among them, organometallic complexes containing Schiff bases have been widely used and investigated with a vast array of metals.

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They are attractive ligands because of their ease of preparation and modification of both steric and/or electronic effects. In 1998, Wang et al. [3] reported the synthesis of several Ni(II) monosalicylaldiminato systems which were highly active for the polymerization of ethylene. The effect of various substituents on the catalytic activity was investigated. Bulky substituents in 3-position of the salicylaldiminato ring were found to enhance the activity of the catalyst as well as an electron withdrawing group in the 5-position, while a relatively electron-rich group in the 5-position decreased the catalytic activity. In 2002, Carliniet al. [4] first reported on the copolymerization of ethylene with methyl methacrylate (MMA) using coordination-type catalysts such as [3,5-dinitro-*N*-(2,6-diisopropylphenyl) salicylaldiminate nickel(II)]. Based on the concept of ligand-oriented catalyst design research, Fujita et al. [5–10] have studied some well-defined titanium complexes featuring non-symmetric fluorinated bis(phenoxy-imine) ligands for olefin polymerization catalysts and found that perfluorinated bis(phenoxyimine) titanium complexes (perfluorinated Ti-FI catalysts) can mediate highly controlled, thermally robust living polymerization of both ethylene and propylene.

UHMWPE has outstanding physical and mechanical properties such as high abrasion resistance, high impact toughness, good corrosion and chemical resistance, resistance to cyclic fatigue, and resistance to radiation [11]. Due to its excellent properties UHMWPE finds use in highly demanding applications [12] including artificial implant materials [13]. The proper choice of catalyst and the appropriate polymerization conditions is crucial for the synthesis of UHMWPE. Low temperature facilitates high molecular weight and fast crystallization of polymer chains. To exclude any interference of molecular weight distribution, we preferred to use a living catalyst system. In a living catalyst chain transfer reactions do not occur and if all catalyst sites start polymerizing simultaneously, a theoretical minimum MWD of 1 can be obtained. The major disadvantage of a living catalyst system is that only one polymer chain is produced by each catalyst site. Matsui et al. [14,15] showed that titanium and zirconium chelates with salicylaldehyde imine ligands exhibit highly catalytic activity in polymerization of olefins and revealed a strong dependence of their catalytic activity on the structure of the aldehyde and amine fragments. Additionally, fluorinated FI catalysts

have been discovered to promote unprecedented living ethylene and propylene polymerizations, resulting in the formation of functionalized polymers and block copolymers from ethylene [16,17]. Our research group also has recently studied ethylene polymerization via bis[*N*-(3,5-dicumylsalicylidene)-2',6'-fluoroanilinato] zirconium(IV) dichloride obtaining polyethylene with high viscosity average molecular weight as a consequence of chain transfer reactions suppression caused by dramatic electronic effect of *ortho*-F substitution on the polymerization mechanism [18]. In continuation of our recent investigation on the synthesis and application of active catalysts for olefin polymerization [19-21], in the present work, we have developed another efficient approach to obtain HMWPE using bis[*N*-(3,5-dicumylsalicylidene)-2',6'-diisopropylanilinato]zirconium(IV) dichloride applying the steric effects of the substitutions. The effects of reaction conditions on the polymerization performance and catalyst activity are examined in detail.

## EXPERIMENTAL

Tetrahydrofuran, dichloromethane, zirconium tetrachloride, phenol and aniline derivatives (Merck, Germany), *n*-butyllithium and methylaluminoxane (as solution in toluene 10%), paraformaldehyde, ethylmagnesium bromide (Sigma Aldrich Chemicals) were used as received. Toluene (Iran, Petrochemical Co) was distilled over calcium hydride and stored over activated 13X and 4A type molecular sieves and sodium wire before use. Other chemicals, polymer characterization and the polymerization procedure explained already [19]. Polymerization of ethylene at low pressure was carried out in a three-necked glass reactor, while higher pressure polymerization was carried out in a 1 L stainless steel Buchi reactor (bcp 250) equipped with controller systems as previously described. Methanol was used as an anti-solvent. The catalyst preparation and polymerization procedure were carried out under atmosphere of dried N<sub>2</sub>. Polyethylene and complex characterization <sup>1</sup>H NMR spectrum was recorded on a Bruker BRX-100 AVANCE spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash 1112EA microanalyzer. Intrinsic viscosity [η] was measured

in decaline at 135°C using an Ubbelohde viscometer.  $M_v$  values were calculated through equation  $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$  [22]. Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10°C/min instrument was used for polymer characterization. The degree of crystallinity of a polyethylene sample was calculated from its heat of fusion which was determined by differential scanning calorimetry. Comparison of the measured heat of fusion with that estimated for 100% crystalline polyethylene yielded the fraction of the sample in a crystal lattice. In practice, the heat of fusion of pure crystalline polyethylene is taken to be in the range of 66-70 cal/g, with a commonly accepted value being 69 cal/g [22,23]. According to the literature [23], calculation of  $DH_f/DH_f^* \times 100$  gives the values of crystallinity where  $DH_f$  is the heat of fusion and  $DH_f^* = 69$  cal/g is the heat of fusion of 100% crystalline polyethylene.

### Synthesis of 3,5-dicumylsalicylaldehyde

The ligand was synthesized according to the literature [15]. To a stirred ethylmagnesium bromide (3.0 M in Et<sub>2</sub>O, 30 mmol) a solution of 2,4-dicumylphenol (in THF, 28.0 mmol) was added dropwise over a 15 min at 0°C. The mixture was stirred for 1 h at room temperature. Dried toluene (50 mL) and a mixture of triethylamine (41.6 mmol) and paraformaldehyde (purity 94%, 93.9 mmol) were added. The mixture was stirred for further 2 h at 80°C. HCl (6 N, 20 mL) was added at 0°C. The organic phase was separated, dried over MgSO<sub>4</sub> and its solvent was removed. The yield of the reaction was about 68%. Anal Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>2</sub>: C, 83.76; H, 7.31; O, 8.93; Found: C, 83.63; H, 7.36; N, 8.89. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz): δ 2.5 (s, 12H, Me), 7.08-7.41 (m, 12H, aromatic-H), 9.70 (s, 1H, CH=O), 11.18 (s, 1H, OH).

### Synthesis of *N*-(3,5-dicumylsalicylidene)-2',6'-diisopropylaniline

To a stirred mixture of 3,5-dicumylsalicylaldehyde (10 mmol) in methanol (50 mL), 2,6-diisopropylaniline (10.50 mmol) was added over a 5 min at room temperature in presence of trace amount of *p*-toluenesulfonic acid as a catalyst. The solution was refluxed for 5 h and after cooling to room temperature the resulting solid was recrystallized from methanol. The yield of the reaction was about 78%. Anal Calcd for C<sub>37</sub>H<sub>43</sub>NO: C, 85.83; H, 8.37; N, 2.71; Found: C,

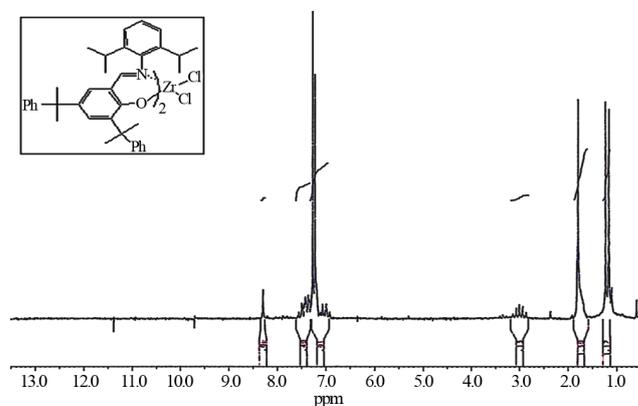
86.12; H, 8.41; N, 2.74. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz): δ 2.02 (d, 12H, Me), 2.36 (s, 12H, Me), 7.05-7.38 (m, 15H, aromatic-H), 8.59 (s, 1H, CH=N), 13.50 (s, 1H, OH).

### Synthesis of bis[*N*-(3,5-dicumylsalicylidene)-2',6'-diisopropylanilinato] zirconium(IV) dichloride

To a stirred solution of *N*-(3,5-dicumylsalicylidene)-2',6'-diisopropylaniline (5 mmol) in dried THF (20 mL) at -78°C, *n*-BuLi (1.6 M in *n*-hexane, 5.5 mmol) was added dropwise in 10 min. The solution was allowed to reach room temperature. Solution of ZrCl<sub>4</sub> (2.5 mmol in THF) was added at 0°C dropwise. The solution was stirred overnight at room temperature. Dried CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added to the solution and mixed for 15 min, the byproduct of LiCl was filtered out. The solid was washed with *n*-hexane and the organic filtrates were added to the solution and concentrated under vacuum to afford a green solid of the catalyst (54%). Anal Calcd for ZrC<sub>74</sub>H<sub>84</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.34; H, 7.08; N, 2.34; Found: C, 75.09; H, 7.12; N, 2.39. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz): δ 1.21 (d, 24H, Me), 1.81 (s, 24H, Me), 3.05 (m, 4H, CH), 7.05-7.55 (m, 30H, aromatic-H), 8.45 (s, 2H, CH=N).

### Ethylene polymerization

All catalyst preparations and polymerization procedures were carried out under dried N<sub>2</sub>. Catalyst handling and polymerization procedures were carried out in 1-L stainless steel Buchi reactor (bcp 250) equipped with controller systems. Toluene (250 mL) was introduced into the nitrogen-purged reactor and stirred (450 rpm) and the reactor was kept at the appropriate temperature and the feeding of ethylene



**Figure 1.** Structure of the prepared FI catalyst of bis[*N*-(3,5-dicumylsalicylidene)-2',6'-diisopropylanilinato]zirconium(IV) dichloride.

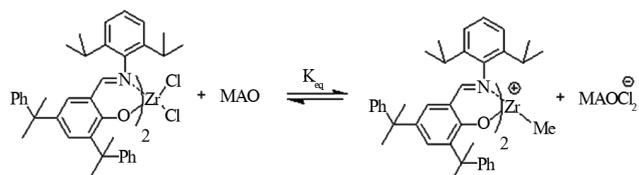
gas (100 L/h) was started.

After 5 min, the ethylene gas feed was stopped and the toluene solution was kept under  $N_2$ . To the resulting toluene solution were added toluene solutions of TIBA, MAO, and catalyst to start ethylene polymerization. Ethylene gas feed was started and the pressure of the reactor was kept constant at the applied monomer pressure for each run. After 15 min, isobutyl alcohol (10 mL) was added and reaction was terminated by shutting off the feed stream followed by nitrogen purge and polymer precipitation using acidified (HCl) methanol. The obtained polymer was recovered by filtration, washed with methanol (100 mL), and dried in a vacuum oven at 70°C overnight. Toluene (250 mL) was used as solvent. MAO was used as the co-catalyst. The catalyst productivity,  $R_p(av)$ , expressed as g PE (mmolZr. h)<sup>-1</sup> was determined after polymerization for specific time for each run.

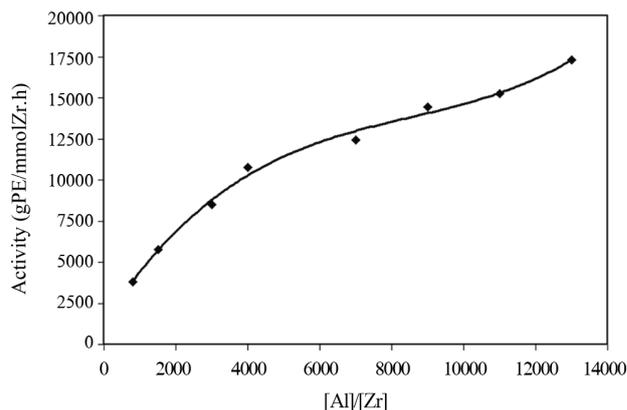
## RESULTS AND DISCUSSION

Polymerization of ethylene was carried out using the catalysts prepared in toluene under different conditions. Since the catalyst was only active in the presence of MAO, the molar concentration of the latter in the medium could affect the activity of the catalyst, when equilibrium reached between the catalyst precursor and the cationic active species formed upon reaction with MAO shown in equation given in Figure 2. It is well-known that besides generating an active cationic metal center, the trimethylaluminum (TMA) present in MAO can cause various side reactions such as chain transfer or deactivation reactions [24]. To study if the molar concentration of methylaluminoxane was effective on the catalyst performance, the effect of co-catalyst to catalyst ratio on the yield and also on molecular weight of the polymers was studied.

The polymerization activity was increased with increasing the [Al]:[Zr] molar ratio in the range studied and no optimum activity was observed (Figure



**Figure 2.** Equilibrium between the catalyst precursor and the active cationic species

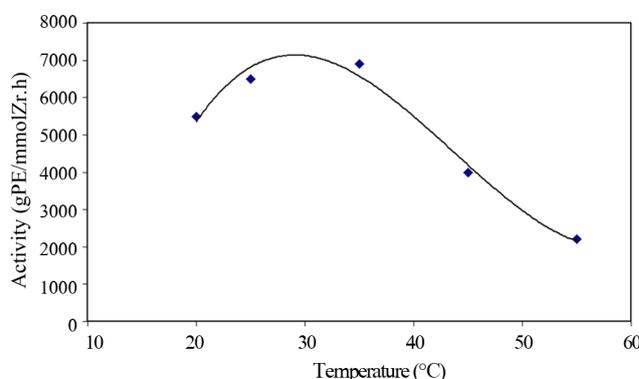


**Figure 3.** Effect of MAO concentration on the average rate of polymerization. Polymerization conditions: temperature= 35°C, polymerization time = 5 min, monomer pressure= 3 bar, [Zr] =  $7 \times 10^{-3}$  mmol, toluene = 250 mL.

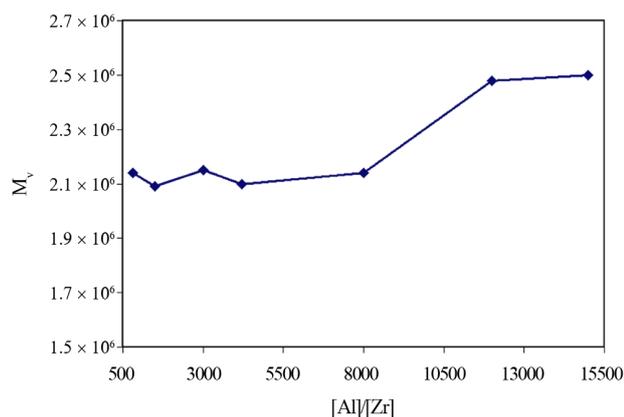
3). The behavior could be due to the existence of bulky substitution groups on the catalyst structure which protected the active centers against chain transfer reaction leading to promotion of the propagation reaction.

Having investigated the trend, because of better results and more logical data on activity, polymerization time was extended to 15 min for further optimization reactions.

The influence of polymerization temperature on the activity was investigated at the temperature between 20 and 55°C, while the [Al]/[Zr] molar ratio was kept constant at [Al]/[Zr]=8000:1. Figure 4 and Table 1 show that up to 35°C, with the increase in temperature, the catalyst activity has increased, resulting in higher yield and higher molecular weight. At 35°C the lower yield and lower molecular weight could have been the result of lower ethylene concentration and increased chain transfer, respectively. In other words, due to



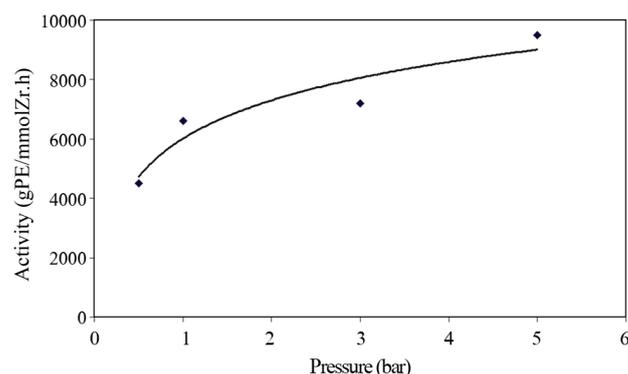
**Figure 4.** Effect of temperature on the average rate of polymerization. Polymerization conditions: polymerization time = 10 min, monomer pressure = 3 bar, [Al]:[Zr] = 8000:1, [Zr] =  $7 \times 10^{-3}$  mmol, toluene = 250 mL.



**Figure 5.** Effect of  $[Al]/[Zr]$  on  $M_n$ . Polymerization conditions: polymerization time = 10 min, monomer pressure = 3 bar,  $[Zr] = 7 \times 10^{-3}$  mmol, toluene = 250 mL.

the oligomeric nature of the MAO, it is not able to deactivate or over reduce the catalyst active centers even at high concentrations.

Figure 5 clearly shows that the catalyst produces HMWPE even at a very high co-catalyst to catalyst ratio. This means that the chain transfer to aluminum is minimal even at such high concentration of trimethylaluminum (in MAO) in the polymerization medium. The obtained molecular weight varies in the range of  $2.15 \times 10^6$  to  $2.5 \times 10^6$  applying  $[Al]/[Zr]$  ratios of 800 to 15000. Therefore, it can be concluded that the catalyst may show living behavior even at high concentration of MAO, strengthening the information reported in the literature that the tert-butyl group at the 3-position of the phenoxy moiety effectively diminishes the probability of chain transfer reactions [25]. However, our previous research on FI-Zr catalysts showed that polydispersity remarkably increased with time and the system started to deviate from pure living behavior [21]. This was either due to the catalyst which did not sustain truly living over the full polymerization period or that the single-site system



**Figure 6.** Effect of monomer pressure on the polymerization activity. Polymerization conditions: polymerization time = 10 min,  $[Al]:[Zr] = 8000:1$ ,  $[Zr] = 7 \times 10^{-3}$  mmol, temperature = 25 °C, toluene = 250 mL.

turned into a multi-site system due to heterogenization of the system. Here we can conclude that bulky substituents on the aniline ring of the phenoxy-imine ligands may invoke strong suppression of  $\beta$ -hydride transfer as well as chain transfer to monomer leading to higher molecular weight.

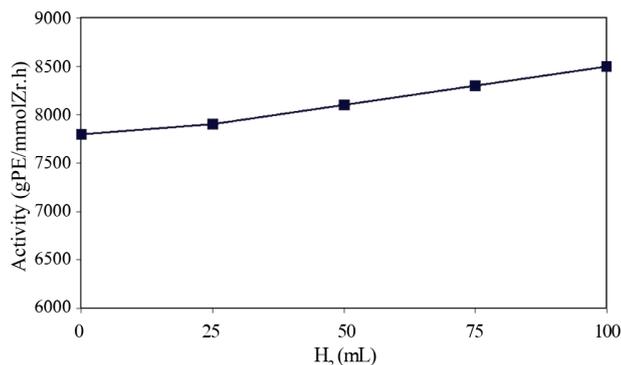
The influence of polymerization pressure on the catalyst in ethylene polymerization is shown in Fig 6. At higher ethylene pressure the coordination and insertion of ethylene become more favorable. Both catalytic activity and polymer molecular weight are significantly promoted under the increasing pressure of 0.5 to 5 bar.

It is evident in Table 1 that the molecular weight of polymer also depends on polymerization temperature. A competition between the termination and propagation steps determines the molecular weight of the polymer. Higher temperature increases the rate of  $\beta$ -hydride chain transfer more than that of the propagation rate and thus affords a polymer with lower molecular weight [21].

Crystallinity and melting point of the obtained polymers are found 55-65% and 115-125°C,

**Table 1** Characterization of the resulting polymer. Polymerization time = 10 min,  $[Al]:[Zr] = 8000:1$ ,  $[Zr] = 7 \times 10^{-3}$  mmol, toluene = 250 mL.

Pressure(bar)	H <sub>2</sub> (mL)	Temperature (°C)	Activity (kg PE/molZr.h)	Crystallinity (%)	Tm (°C)	M <sub>n</sub>
0.5		25	4.5	60	125	-
1	-	25	6.6	60	128	$1.10 \times 10^6$
3	-	25	7.2	63	130	$2.14 \times 10^6$
5		25	9.5	65	135	$2.77 \times 10^6$
3		45	2.3	60	130	$1.12 \times 10^6$
3		55	1.5	55	133	$0.88 \times 10^6$
3	25	25	7.9	-	133	$2.13 \times 10^6$
3	50	25	8.10	63	131	$2.13 \times 10^6$
3	75	25	8.15	62	131	$2.13 \times 10^6$
3	100	25	8.50	63	131	$2.12 \times 10^6$

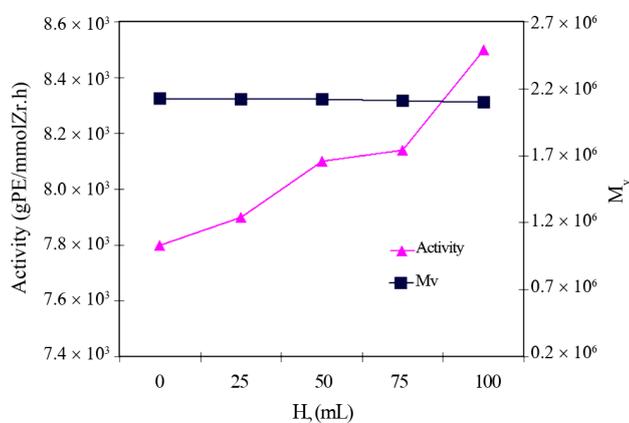


**Figure 7.** H<sub>2</sub> versus activity. Polymerization conditions: polymerization time = 10 min, [Al]:[Zr] = 8000:1, [Zr] =  $7 \times 10^{-3}$  mmol, temperature = 35°C, toluene = 250 mL.

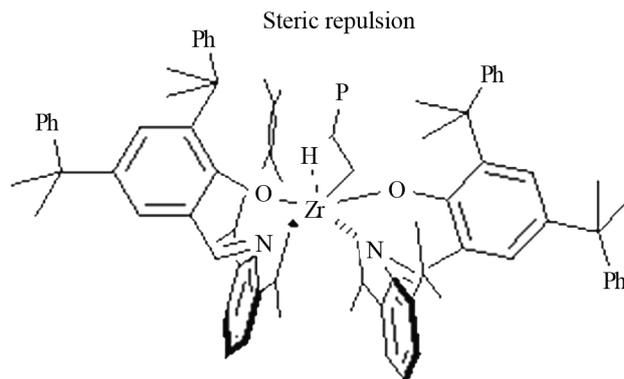
respectively. Higher pressure increased both the crystallinity and the  $M_v$  values of the resulting polymer. Table 1 shows some specifications of the obtained polyethylene using the catalysts.

Ethylene polymerization was carried out using different amounts of hydrogen as a chain transfer agent. Activity of the catalysts was slightly influenced by hydrogen concentration. As it can be seen in Figures 7 and 8 higher amounts of hydrogen could only slightly increase the activity of the catalysts without significant effect on molecular weight of polymer. It is presumably the bulky alkyl substitutions which probably prevent hydrogens taking close to the active centers. In this respect, our research group has proposed a reasonable working mechanism for reactivation of active centers by hydrogen which would result in increased catalysts activity [26].

At the monomer pressures of 3 and 5 bar, the prepared FI catalyst produced polyethylene with  $M_v$  value of



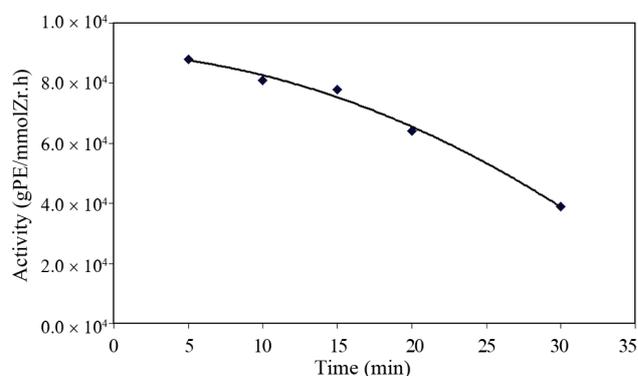
**Figure 8.** Influence of hydrogen concentration on the catalyst activity and  $M_v$  of the obtained polymer. Polymerization time = 10 min, [Al]:[Zr] = 8000:1, [Zr] =  $7 \times 10^{-3}$  mmol, temperature = 35°C, toluene = 250 mL.



**Figure 9.**  $\beta$ -agostic interaction: steric repulsion between  $\beta$ -hydrogen of the growing polymer chain and isopropyl alkyl substitutions phenyl ring on the N

$2.14 \times 10^6$  to  $2.77 \times 10^6$ , respectively. Bulky cumyl group at the *ortho* position of the phenoxy oxygen as well as the 2,6-diisopropyl substituted phenyl ring on the ligand can promote chain propagation, though they do decrease the activity of the catalyst intensively. In other words, as demonstrated in Figure 9, it seems that the  $\beta$ -carbon of the polymer chain is not easily accommodated in the plane because of the steric interaction between phenoxy-imine ligands of the catalyst and  $\beta$ -H of the growing polymer chain. It can be concluded that the sterically bulky substituents on the aniline ring of the phenoxy-imine ligands cause a strong suppression of  $\beta$ -hydride elimination to undergo chain propagation reaction.

High  $M_v$  was obtained at the expense of reduced catalyst activity due to overwhelming steric congestion around the catalyst structure derived from bulky substitutions. The kinetics of the polymerization is shown in Figure 10. Ethylene polymerization was carried out at different reaction times while the [Al]/[Zr] molar ratio and the polymerization temperature were kept constant. The  $R_p$ /time profile showed a



**Figure 10.**  $R_p$  versus time. Polymerization conditions: pressure = 3 bar, [Al]:[Zr] = 8000:1, [Zr] =  $7 \times 10^{-3}$  mmol, toluene = 250 mL

decay type. The catalytic activity reached its maximum quickly at the beginning of the polymerization. Then, the activity decreased dramatically and after 30 min the activity was quite low.

## CONCLUSION

The bulky substitution on a FI catalyst structure not only provided steric protection for the phenoxy-oxygen against electrophilic attack by the co-catalyst which probably sustained its activity even at higher ratio of  $[Al]/[Zr]$ , but it also had a substantial effect on  $M_v$  of the obtained polymer. This behavior indicated the presence of a dramatic steric effect of the substitutions on the catalyst performance. The prepared Zr-based FI catalysts could produce high molecular weight polyethylene, though due to overwhelming steric congestion derived from bulky substitutions in the catalyst, the activity of the catalyst was decreased. Polymerization activity was increased with increases in both monomer pressure and  $[Al]/[Zr]$  molar ratio. Higher pressure increased productivity, crystallinity and the  $M_v$  values of the resulting polymer. Higher hydrogen concentrations just slightly affected the activity of the catalysts to higher values.

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