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Highly Active FI Catalyst of Bis[*N*-(3,5-dicumylsalicylidene) cyclohexylaminato]zirconium(IV) Dichloride for Polymerization of Ethylene

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ABSTRACT

A highly active Zr-based FI catalyst of bis[*N*-(3,5-dicumylsalicylidene)cyclohexylaminato]zirconium(IV) dichloride was prepared and used for polymerization of ethylene. The catalyst displayed a very high activity of about 3.2×10^6 in ethylene polymerization at the monomer pressure of 3 bar using triisobutylaluminium (TIBA) and methylaluminoxane (MAO) as a scavenger and cocatalyst, respectively. The highest activity of the catalyst was obtained at about 35°C. The polymerization activity was increased linearly with increased monomer pressure and [Al]:[Zr] ratio in the range studied. Introduction of bulky cumyl group on *ortho* position to the phenoxy oxygen prevents the catalyst from coordination to the cocatalyst following its easier coordination of ethylene to the active centres. The existence of bulky substitutions on the catalyst structure resulted in linear increase in its activity with increasing the MAO concentration through ion separation which facilitates the monomer insertion. However, fouling of the reactor was strongly increased with monomer pressure and the amount of MAO used. Ethylene polymerization was carried out using different amounts of hydrogen. The activity of the catalyst was slightly increased with addition of hydrogen; however, the viscosity average molecular weight ($\overline{M}_v$) of the obtained polymer was not affected. In order to study the catalyst lifetime service, ethylene polymerization reactions were carried out at different reaction times while the temperature and [Al]/[Zr] molar ratio were kept constant. Despite the high activity, the catalyst showed a short lifetime. Crystallinity and melting point of the obtained polymer were between 55-65% and 125-130°C, respectively. $\overline{M}_v$ values of the obtained polymer were dropped as polymerization temperature increased, while higher pressure increased both the crystallinity and the $\overline{M}_v$ values of the resulting polymer. Meanwhile some specifications of the obtained polymer were investigated.

Key Words:

FI catalyst;
Zr-based catalyst;
catalytic polymerization;
olefin polymerization;
polyethylene.

INTRODUCTION

Development of new catalysts with transition metals has played a substantial role in the fast-growing polyolefins industry. Following Ziegler-Natta catalysts [1], metallocene catalysts were discovered in the 1980s and resulted in numerous industrial processes for improving the properties of polyolefinic materials along with performance parameters [2]. The interest in polymerization of olefins has increased recently due to the observed catalytic activity of Schiff base complexes in the synthesis of commercially important branched [3,4] and linear polyethylenes [5-8]. Recently much attention has been paid to the non-metallocene catalysts [7-11]. This is because

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these complex catalysts exhibit unique characteristics for production of new polymers that are not prepared by conventional Ziegler-Natta catalysts, as well as by ordinary metallocene type and or "constrained geometry" (linked Cp-amide) type catalysts [11]. A new class of olefin polymerization catalysts based on the group 4 transition metals having two phenoxy imine chelate ligands, named FI catalyst which has been invented by Fujita has raised steady interest [12]. The FI catalysts display a very high ethylene polymerization activity using methylaluminoxane (MAO) as a cocatalyst at ambient temperature. FI catalysts have been found to produce various new polymers such as low molecular weight polyethylene, ethylene-propylene copolymer and ultra high molecular weight polyethylene [13-15]. Polymerization behaviour using FI catalysts have indicated that in these classes of catalysts minor changes in the ligand structures can have a significant effect on the activity of the catalyst [14-20]. Depending on the ligand design, the catalysts show different behaviours in ethylene and propylene polymerization, and the ligands strongly influence catalyst parameters such as activity, polymerization mechanism, and polymer properties including molecular weight [20]. For instance, FI catalyst requires steric congestion close to the polymerization active centre in order to exhibit high ethylene polymerization activity [17,18].

Although many FI catalysts have been tried out for ethylene polymerization and data for activities have been reported, but less attention has been paid to the catalyst behaviour during the polymerization. Thus, investigation of ethylene polymerization behaviour using FI catalysts would be highly desirable. In the present work, a Zr-based FI catalyst was synthesized and used for polymerization of ethylene. The catalyst showed high activity for ethylene polymerization. A specific interest we have in mind is to find a high active FI catalyst and then investigate the ligand electronically and steric effects on the catalyst behaviour during the polymerization. Therefore, after screening some FI catalysts, we found out that the bis[*N*-(3,5-dicumylsalicylidene) cyclohexylaminato]zirconium(IV) dichloride, among the tested catalysts in our laboratory displays the highest activity for ethylene polymerization. Then, we focused on the catalyst behaviour during the polymerization to obtain the best conditions to reach the highest activity of the catalyst. As the catalytic performance is sensitive to the conditions of polymerization which is influenced by factors such as temperature, monomer concentration, catalyst/cocatalyst molar ratio and time of polymerization, the above parameters were investigated intensively. The influence of hydrogen concentration on the polymerization activity was investigated. Also some specifications of the resulting polymer were studied.

EXPERIMENTAL

Zirconium tetrachloride, dichloromethane, methanol, 4-toluenesulphonic acid, phenol and amine derivatives were supplied by Merck Chemicals (Darmstadt, Germany) and were used as received. Toluene was obtained from Merck Chemicals, *n*-hexane was supplied by Arak Petrochemical Co. (Arak, Iran), the chemicals were prepared from distilling over sodium wire, stored over 13X and 4A activated molecular sieves and degassed by bubbling with dried nitrogen gas before use. Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical Co. (Tehran, Iran). Nitrogen gas (purity 99.99%) was supplied by Roham (Tehran, Iran). Methylaluminoxane (MAO) (10% solution in toluene) and triisobutylaluminium (T1BA) (purity 93%) were supplied by Sigma Aldrich Chemicals (Steinheim, Germany). Catalyst handling and polymerization procedures were carried out in a 1-L stainless steel Buchi reactor (bcp 250) equipped with controller system as previously described [21,22]. Toluene (250 mL) was introduced in to the reactor and stirred (600 rpm) under a N_2 atmosphere. The toluene was kept at the appropriate temperature and then the ethylene gas feed was started. TIBA, MAO and the catalyst were introduced into the reactor containing toluene under a positive pressure of ethylene, respectively. After 10 min, by shutting off the feed stream and addition of *sec*-butyl alcohol (10 mL) polymerization was terminated. The resulting mixture was poured into acidic methanol (1000 mL containing 2 mL of concentrated HCl). The polymer was collected by filtration, washed with methanol and then dried in vacuum at 80°C for 8 h.

Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10°C/min instrument was used for polymer characterization. The viscosity average molecular weight ($\overline{M}_v$) and crystallinity of some polymer samples were determined according to the literature [21,23,24]. Intrinsic viscosity [η] was measured in decaline at 135°C using an Ubbelohde viscometer. $\overline{M}_v$ values were calculated through equation $[\eta] = 6.2\times10^{-4}\,\overline{M}_v^{0.7}$ [23]. All the catalyst preparation and polymerization procedures were carried out under dried N_2. ^1H NMR Spectrum was recorded on a Bruker BRX-100 Avance Spectrometer. The peak melting temperature (T_m) of the polymers was determined by DCS (Universal V4IDTA) while reheating the polymer sample to 200°C at a heating rate of 10°C/min. Elemental analysis for CHN was carried out by CHNO type Thermo Firingan 11112EA Microanalyzer. Due to extreme air sensitivity of the catalyst and also lack of suitable apparatus, we could not study the XRD of the catalyst.

Synthesis of 3,5-Dicumylsalicylaldehyde

To a stirred ethylmagnesium bromide (3.0 M in Et_2O, 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 2 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 and HCl (6 N, 20 mL) was added at 0°C. The organic phase was separated, dried over $MgSO_4$ and its solvent was removed. The yield of the reaction was about 65%. ^1H NMR ($CDCl_3$, 100 MHz): δ 2.5 (s, 12H, Me), 7.08-7.41 (m, 12H, aromatic-H), 10.14 (s, 1H, CH=O), 12.97 (s, 1H, OH).

Synthesis of *N*-(3,5-Dicumylsalicylidene)cyclohexylamine

To a stirred mixture of 3,5-dicumylsalicylaldehyde (10 mmol) in CH_2Cl_2 (50 mL), cyclohexylamine (10.5 mmol) was added over a 5 min at room temperature in the presence of a trace amount of 4-toluenesulphonic acid as a catalyst. The solution was refluxed for 2 h, concentrated and the resulting solid was recrystallized from methanol to obtain yellow crystals. The yield of the reaction was about 78%. ^1H NMR ($CDCl_3$, 100 MHz): δ 1.10-1.30 (m, 10H, cyclohexyl), 1.70 (s, 12H, Me), 3.05 (m, 1H, CH-N), 6.90-7.41 (m, 12H, aromatic-H), 8.20 (s, 1H, CH=N), 13.50 (s, 1H, OH), (Figure 1). Anal. Found; C, 84.84; H, 8.68; N, 3.35. Calcd. for $C_{31}H_{37}NO$: C, 84.69; H, 8.48; N, 3.19.

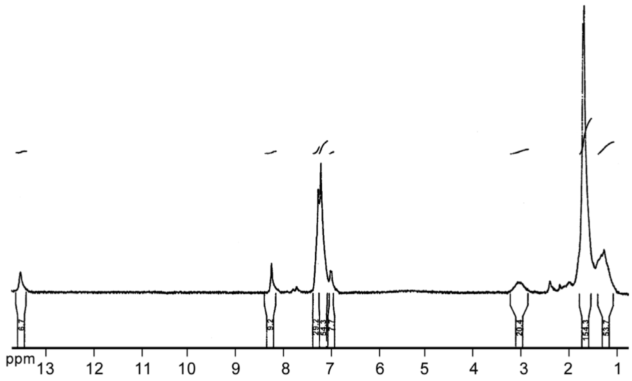


Figure 1. NMR of ligand.

Synthesis of Bis[*N*-(3,5-dicumylsalicylidene)cyclohexylaminato]zirconium(IV) Dichloride

To a stirred solution of *N*-(3,5-dicumylsalicylidene) cyclohexylamine (5 mmol) in dried THF (20 mL) at -78°C, *n*-butyllithium (1.6 M in *n*-hexane, 5.2 mmol) was added dropwise in 10 min. The solution was allowed to warm to room temperature. Solution of $ZrCl_4$ (2.5 mmol in THF) was added at 0°C dropwise. The solution was stirred for 16 h at room temperature. Dried CH_2Cl_2 (50 mL) was added to the solution and mixed for 15 min, the by-product of LiCl was filtered. The solid residue was washed with dry CH_2Cl_2 (15 mL × 3) and the combined organic filtrates were concentrated in vacuo to afford a pale yellow solid. Diethyl ether (30 mL) and *n*-hexane (50 mL) were added to the solid and the mixture was stirred for 1 h and then filtered. The resulting solid washed with *n*-hexane (10 mL × 3) and dried in vacuum to give the catalyst as a yellow solid in 68% yield. ^1H NMR (CD_2Cl_2, 100 MHz): δ 1.50-1.95 (m, 20H, cyclohexyl), 1.86 (s, 24H, Me), 3.30 (m, 2H, CH-N), 6.90-7.55 (m, 24H, aromatic-H), 8.05 (s, 2H, CH=N), (Figure 2). Anal. Found; C, 71.79; H, 7.21; N, 2.58. Calcd. for $ZrC_{62}H_{72}N_2O_2Cl_2$: C, 71.88; H, 7.35; N, 2.62. The procedure adopted in the synthesis of the catalyst is outlined in Scheme I.

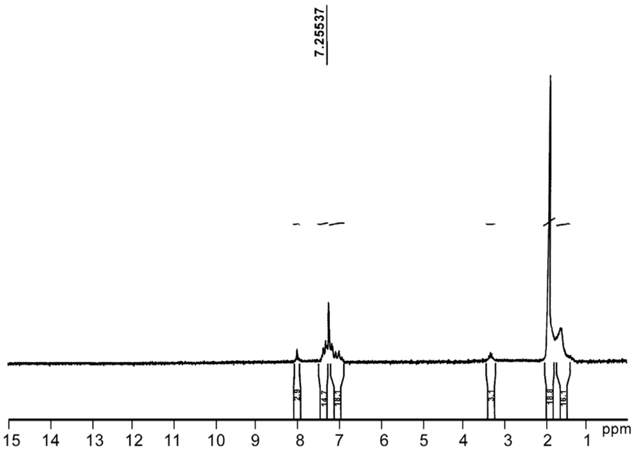


Figure 2. NMR of catalyst.

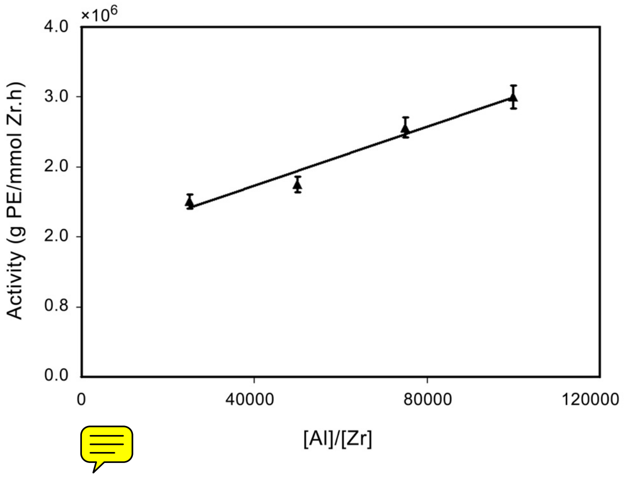
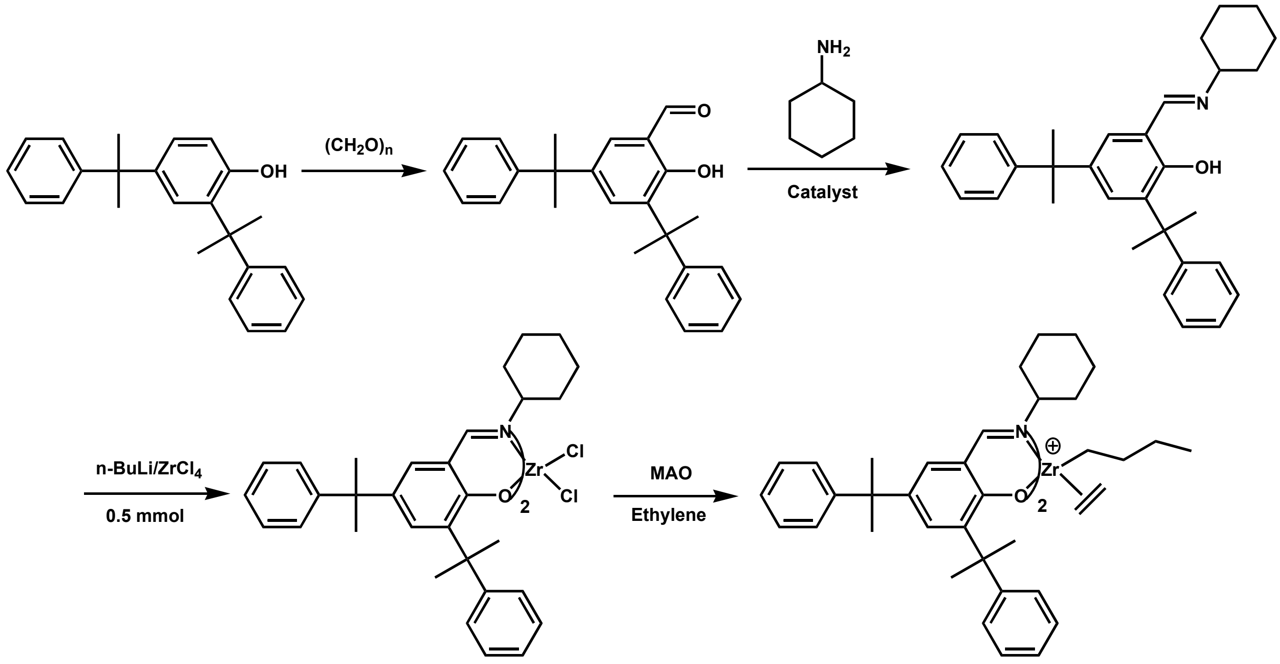


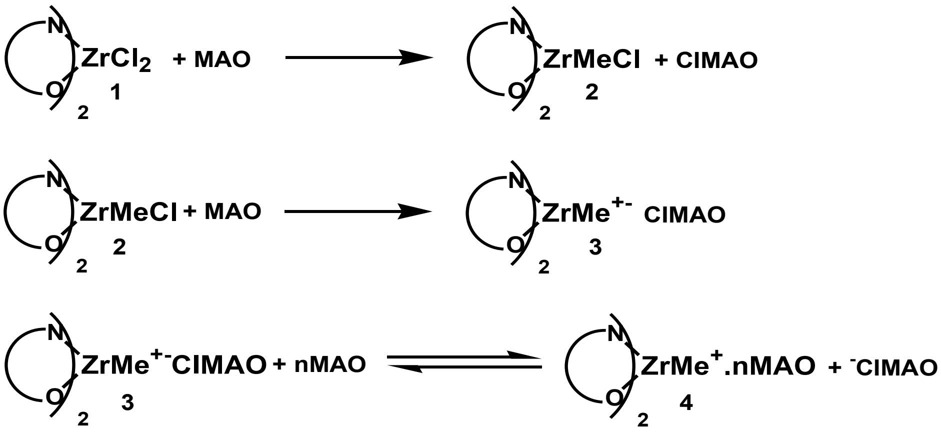
Figure 3. Effect of MAO concentration on the average rate of polymerization. Polymerization conditions: [Zr] = 0.02 mmol, temperature = 35°C, time = 10 min, monomer pressure = 3 bar, toluene = 250 mL.

RESULTS AND DISCUSSION

Polymerization of ethylene was carried out using the prepared catalyst under different conditions in toluene. The catalyst productivity, R_p (average) is expressed as g PE $(\text{mmol Zr.h})^{-1}$ was determined after polymerization for 10 min for each run (as reported in literature [17]). TIBA (2 mmol) (the scavenger) was added prior to the addition of MAO (the cocatalyst). It should be noted that the value of aluminium in [Al]:[Zr] molar ratio comes from MAO as a cocatalyst, while TIBA was only considered as a scavenger. The polymerization activity was continuously increased with increasing the [Al]:[Zr] molar ratio in the range studied (Figure 3). The behaviour confirms that chain transfer to the aluminium compound does not play a dominant role in the chain termination. It is already well-established



Scheme I. Synthetic route to prepare bis[*N*-(3,5-dicumylsalicylidene)cyclohexylaminato]zirconium(IV) dichloride (FI) catalyst.



Scheme II. Effect of MAO on ion pair separation and catalyst activation.

that a high excess of MAO is necessary to accomplish high polymerization activities. Similar results have been reported in the literature for homogeneous metallocene systems [25,26] in which activity grows with increasing Al/Zr molar ratios. The requirement for great amount of MAO can be explained by the equations which are shown in Scheme II [27]. Since MAO exists in large amount, MAO molecules may act as solvating molecules for the cation leading to separation of the ion pair (3). The new species, the metallic cation solvated by MAO (4), is expected to be more active than the contact ion pair (3) and much more stable than the free cation solvated only by the solvent (toluene). This and the low value found for the equilibrium constant of the last equation may explain why the catalyst systems with MAO are much more active than those using alkylaluminium as cocatalyst and why such a large excess of MAO is necessary to obtain high activities. Therefore, in the present study the molar ratio of [Al]/[Zr] = 100000:1 was used for further polymerization reactions, however, the use of a large ratio of [Al]/[Zr] = 125000:1 has been applied to reach the highest activity of FI catalyst of bis[*N*-(3-tert-butylsalicylidene)anilinato]zirconium (IV) dichloride [28].

It has been reported that the sterically bulky substitution on *ortho* position to the phenoxy oxygen of the ligand provides steric protection towards the anionic phenoxy oxygen from coordination with Lewis acid compounds [29]. In the prepared catalyst, existence of bulky cumyl group on *ortho* position to the phenoxy oxygen prevents the catalyst from coordination to the cocatalyst and subsequent chain transfer reactions, even at higher concentration of the cocatalyst, following the easier coordination of ethylene to the active centres, possibility of insertion reaction to take place more than the chain transfer reactions and ultimately causes the activity of the catalyst to increase [29,30].

It should be pointed out that the minor change in the structure of the FI catalysts leads to the major changes in activities as well as molecular weight and other characteristics of the resulting polymer. In addition, due to the specific polymerization conditions used in this work for ethylene polymerization such as the amount of cocatalyst/catalyst, polymerization temperature and monomer pressure, and also due to the high sensitivity of FI catalysts to the applied polymerization conditions, the reported data for overall activities might have tolerance w those reported in the literatures.

The influence of polymerization temperature on activity was studied at temperatures between 20°C and 55°C, while the [Al]/[Zr] molar ratio was kept constant at [Al]/[Zr] = 100000:1. As it is evident in Figure 4, the highest activity of the catalyst was obtained at 35°C. The reduction in catalyst activity in the polymerization performed at the lower and upper temperatures than the optimum value could be attributed to a low propagation rate and catalyst irreversible deactivation, respectively [31]. At low polymerization temperatures the π-olefin complex is more stable and its lifetime is greater than the rate of insertion. On the other hand, for high polymerization

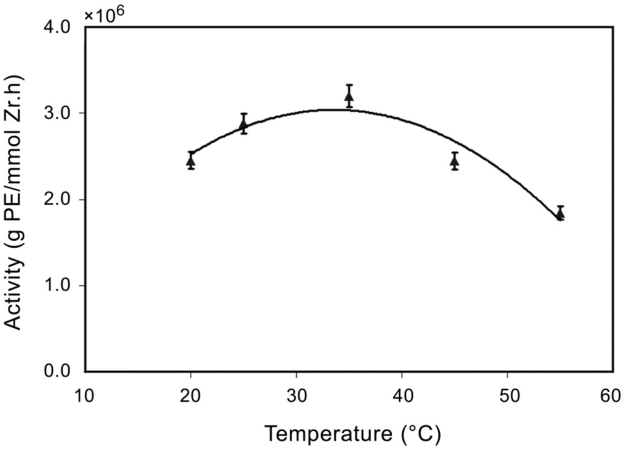


Figure 4. Effect of temperature on the average rate of polymerization. Polymerization conditions: [Zr] = 0.02 mmol, time = 10 min, monomer pressure = 3 bar, [Al]:[Zr] = 100000:1, toluene = 250 mL.

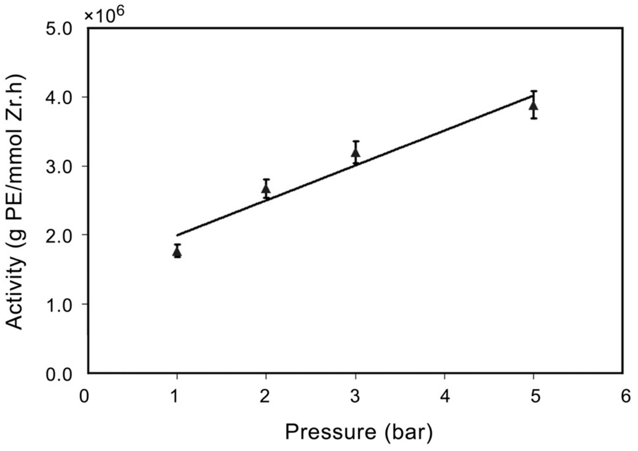


Figure 5. Effect of monomer pressure on the polymerization behaviour. Polymerization conditions: [Zr] = 0.02 mmol, toluene = 250 mL, temperature = 35°C, other conditions as in Fig 4.

temperature, the π-olefin complex is unstable and readily dissociates. In other words, the olefin polymerization rate is expected to increase with the temperature, but the trend is reversed at high temperature due to catalyst decomposition which occurs at high temperature. However, higher temperature promotes easy transfer of the monomer to the catalytic active centres [32]. Meanwhile, solubility of the monomer gas in the polymerization medium decreased with increasing temperature. Similar trend was already mentioned in the literature using homogeneous *ansa*-metallocene catalysts [33,34].

The influence of monomer pressure between 1 and 5 bar on the catalyst behaviour was studied. The polymerization behaviour is shown in Figure 5. The higher the pressure of the monomer, the higher the activity of the catalyst observed. The behaviour is mainly due to high concentration of the monomer close to the catalyst active centres [34]. It should be noted that fouling was observed even at low monomer pressure due to the homogeneous nature of the polymerization. Fouling of the reactor was increased with increasing both of the monomer pressure and MAO concentration, and the polymer obtained was deposited on the whole reactor wall and the fouling was obviously remarkable.

To study the catalyst lifetime, ethylene polymerization was carried out for 5, 10, 15 and 20 min for the reaction carried out at 35°C and at constant [Al]/[Zr] ratio. The results indicated that in spite of very high polymerization activity, the catalyst has a short catalytic lifetime (Figure 6). As catalyst lifetime is a substantial factor in this scope, ethylene polymerization was carried out with prolonged reaction time in order to ascertain the lifetime of the catalyst. At prolonged reaction time, catalyst activity was dramatically diminished and the catalyst activity was negligible after 45 min of the reaction and no more polymers were obtained. The behaviour of the catalyst is attributed to its short lifetime under the conditions employed which is 45 min.

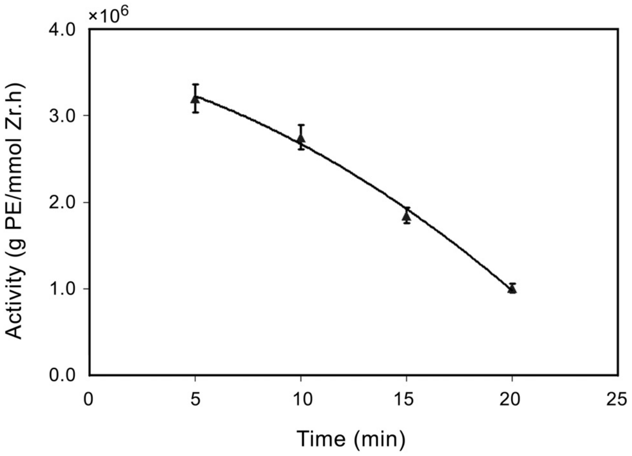


Figure 6. Plot of R_p versus time. Polymerization conditions: temperature = 35°C, other conditions as in Figure 4.

Table 1. Characterization of the resulting polymer using the prepared catalyst.

Pressure (bar)	H_2 (mL)	Temperature (°C)	Activity (g PE/mmol Zr.h)	Crystallinity (%)	T_m (°C)	$\overline{M}_v$
1	-	35	1.77×10^6	57	128	1.61×10^4
3	-	35	3.21×10^6	63	130	1.95×10^4
5	-	35	3.92×10^6	65	130	2.37×10^4
3	-	45	2.44×10^6	60	128	1.32×10^4
3	-	55	1.84×10^6	55	125	0.97×10^4
3	25	35	3.20×10^6	63	133	1.94×10^4
3	50	35	3.30×10^6	61	131	1.95×10^4
3	100	35	3.37×10^6	61	130	1.94×10^4

The effect of polymerization temperature on the viscosity average molecular weight ($\overline{M}_v$) is illustrated in Table 1. It may be seen that, $\overline{M}_v$ values are decreased as polymerization temperature increased. Similar behaviours have been reported in the literature [21,34]. At lower temperatures, propagation is favoured over termination and the resulting polymer has higher molecular weight. On the other hand, higher temperature supplies the activation energy requirement for chain transfer reactions, especially β-hydride elimination which results in lower polymer molecular weight [35].

Ethylene polymerization was carried out using different amounts of hydrogen while the optimum temperature was applied as obtained before. The $\overline{M}_v$ of the obtained polymer was not affected with hydrogen concentration. However, activity was slightly increased using higher amount of hydrogen (Figure 7). Similar results have been reported [36].

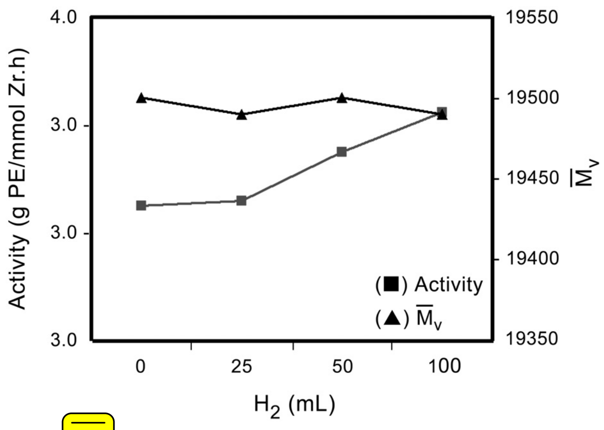


Figure 7. Influence of the hydrogen concentration on the polymerization activity and $\overline{M}_v$. Polymerization conditions as in Figure 6.

Crystallinity and melting point of the obtained polymers were between 55-65% and 125-130°C, respectively. Higher pressure increased both the crystallinity and the $\overline{M}_v$ values of the resulting polymer (Table 1).

CONCLUSION

The prepared bis[*N*-(3,5-dicumylsalicylidene) cyclohexylaminato]zirconium(IV) dichloride/MAO catalyst system displayed a very high activity for polymerization of ethylene. The highest activity of the catalyst was obtained at about 35°C, while, the activity increased with addition of [Al]/[Zr] molar ratio and monomer pressure and no optimum activity was observed in the range studied. However, fouling of the reactor was strongly increased with increasing both of the monomer pressure and the amount of MAO used. Higher monomer pressure increased both the crystallinity and the $\overline{M}_v$ values of the resulting polymer. Addition of hydrogen slightly increased the activity of the catalyst, while molecular weight was insensitive to hydrogen concentration. Despite such high activity, this catalyst showed a short lifetime.

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