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ORIGINAL PAPER

FI Zr-type catalysts for ethylene polymerization

Saman Damavandi · Griselda Barrera Galland · Gholam Hossein Zohuri · Reza Sandaroos

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Abstract Two FI-type catalysts of Bis[N-(3,5-dicumylsalicylidene)-naphthylaminato]zirconium(IV) dichloride (catalyst (a)) and Bis[N-(3,5-dicumylsalicylidene)-anthracylaminato] zirconium(IV) dichloride (catalyst (b)) were prepared and used for ethylene polymerization comparatively. Methylaluminoxane (MAO) was used as cocatalyst. Polymerization reactions of ethylene using the prepared catalysts at the different conditions of polymerization were carried out. Plurality of the fused aromatic rings on the N atom of the imine in the catalyst structure affected the polymerization activity and molecular weight of the resulting polymer as well. Productivity of the prepared catalysts increased with the addition of [Al]/[Zr] molar ratio. The highest activity was observed at about 35–40 °C for the catalysts. The catalyst (b) produced higher viscosity average molecular weight (M_v) of the obtained polyethylene, while generally the activity of the catalyst (a) was higher than the catalyst (b). Similar behavior was observed for the polymerization carried out at the monomer pressure of 2 to 6 bars using the catalysts. The higher the pressure the more activity of the catalysts obtained, in the range studied. Crystallinity and melting point of the obtained polymer were between 55–65% and 120–135 °C respectively. Higher pressure increased both the crystallinity and the M_v values of the resulting polymer. The polymerization was carried out using different amounts of hydrogen. Higher amount of hydrogen could increase the activity of the catalysts. A linear dependence between the polymerization time and the molar weight was observed, however the polydispersity was broadened with the time.

Keywords Catalytic polymerization · FI catalyst · Zr-based catalyst · Olefin polymerization · Polyethylene

Introduction

Ziegler-Natta catalysts have been developed to achieve higher productivities and better stereoselectivity. The current state-of-the-art Ziegler-Natta catalyst comprises of $MgCl_2$ support, $TiCl_4$, aluminium alkyl(s) and internal- and/or external-donor (s) [1–3]. Even though the performance of Ziegler-Natta catalysts have been greatly improved, they have an inherent characteristic of being “multisite” catalysts, i.e. the environment around the active sites varies resulting in broad molecular weight distributions as well as variations in stereoselectivity. Well-defined, homogeneous, “single-site” catalysts provide a solution for this drawback of heterogeneous Ziegler-Natta catalysts. Following the great success of the metallocene catalysts, significant efforts have been directed towards the discovery and application of new, highly active, single-site catalysts (post-metallocene catalysts) [4, 5]. These research efforts have led to the introduction of quite a few high-activity, single-site catalysts based on both early and late transition metal complexes with various ligand environments [6–14].

A new series of non metallocene FI catalysts have been reported by researchers from Mitsui Chemicals which polymerize ethylene and propylene in conjunction with methylaluminoxane (MAO) as an activator at ambient temperature [15]. FI catalysts are very versatile. They are

S. Damavandi (✉) · G. H. Zohuri · R. Sandaroos
Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran
e-mail: Saman_Damavandi@yahoo.com

G. B. Galland
Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

more tolerant to functional groups and produce polymers of variable structures, ranging from linear crystalline to highly branched amorphous polymers. In addition, the catalyst system contain zirconium complexes are capable of producing polyethylene of low to very high molecular weight polymer by changing the ligands structure. It has been claimed that substitution position has profoundly effect on activity of the catalyst [16–18].

However, salicylaldimines had been utilized initially by Grubbs and co-workers as ligand precursors for nickel catalysts used in ethylene polymerisation [5]. They provided neutral ethylene polymerization catalysts not requiring aluminum or boron activators, showing high activity and increased tolerance versus polar species [19].

Although a large number of families of high-performance single-site catalysts have been developed thus far, improvements in some aspects of catalytic performance (e.g., temperature stability, precise control of chain transfer, comonomer sequence distribution control, precise control of polymer stereochemistry, and the ability to incorporate sterically encumbered monomers and polar monomers) are still required in order to achieve both greater control over polymer microstructures and extension of generic polyolefinic materials by introducing new monomer combinations.

In the present work, two new Zr-based FI catalysts were synthesized by changing the ligand structure, salicylaldimines moiety, and used for ethylene polymerization. The catalytic performance is influenced by factors such as reaction temperature, monomer pressure, catalyst/co-catalyst molar ratio and hydrogen concentration. A specific interest was concerned to investigate the ligand electronic and steric effects on the catalyst activity and to figure out a correlation between catalyst structure and catalyst activity which can be revealed by polymerization. Some specification of the resulted polymer was studied.

Experimental

Materials and characterization

Zirconium tetrachloride, dichloromethane, methanol, 4-toluenesulfonic acid, phenol and aminoanthracene derivatives were supplied by Merk Chemical (Darmstadt, Germany) and were used as received. Toluene was obtained from the 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 (Tehran, Iran). Nitrogen gas (purity 99.99%) was supplied by Roham (Tehran Iran). Methylaluminoxane (MAO) (10% solution in toluene) was supplied by Sigma Aldrich Chemicals (Steinheim, Germany). Catalyst handling and polymerization procedures were carried out in 1-L stainless steel Buchi reactor (bcp 250) equipped with controllers systems as described elsewhere [20]. MAO and catalyst were respectively introduced in the reactor containing toluene under a positive pressure of ethylene. After 15 min, reactions were terminated by shutting off the feed

Catalyst (**a**) Catalyst (**b**)

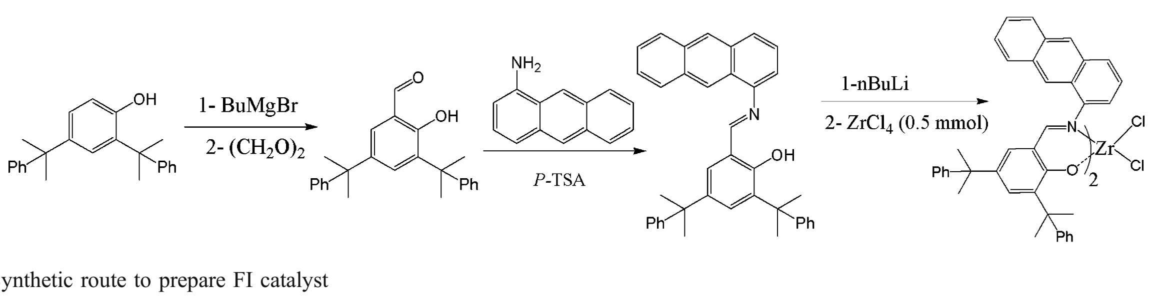


Fig. 1 Synthetic route to prepare FI catalyst

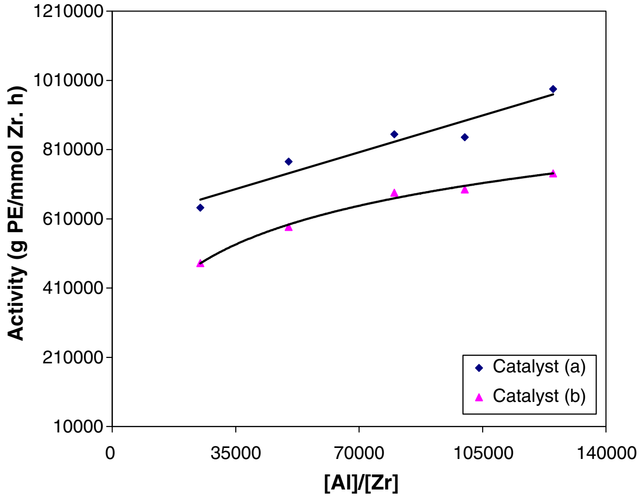


Fig. 2 Effect of MAO concentration on the average rate of polymerization. Polymerization conditions: temperature=30°C, polymerization time=15 min, monomer pressure=2 bar, [Zr]=0.02 µmol, toluene=250 ml

stream, followed by nitrogen purge and polymer precipitation using Acidified (HCl) ethanol. TIBA was used as scavenger and added to the reactor before addition of the MAO. The polymer was precipitated and dried at 80°C for overnight. Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10°C/min and gel permeation chromatography (GPC) (Waters, Milford, MA 2000) instruments were used for polymer characterization. The degree of crystallinity of a polyethylene sample can be calculated from its heat of fusion which can be determined by differential scanning calorimetry. Calculation of $Hf/Hf^{*} \times 100$ gives the values of crystallinity where Hf is the heat of fusion and $Hf^{*}=69$ cal/g is the heat of fusion of 100% crystalline polyethylene [21]. The peak melting temperature (Tm) 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. Intrinsic viscosity [η] was measured in decaline at 135°C using an Ubbelohde viscometer. Mv values were calculated through equation $[\eta]=6.2\times10^{-4}\,Mv^{0.7}$ [22]. All the catalyst preparation and polymerization procedure

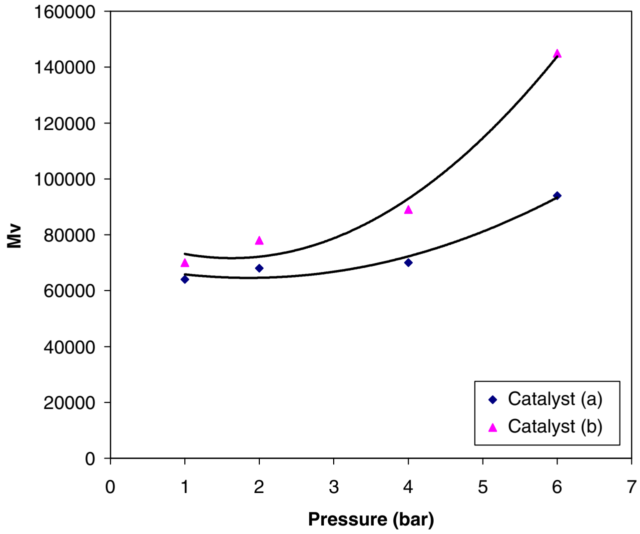


Fig. 3 Viscosity average molecular weight (M_v) of the polymer versus monomer pressure. Polymerization conditions: polymerization time=15 min, temperature=35°C, [Al]:[Zr]=80000:1, [Zr]=0.02 µmol, toluene=250 ml

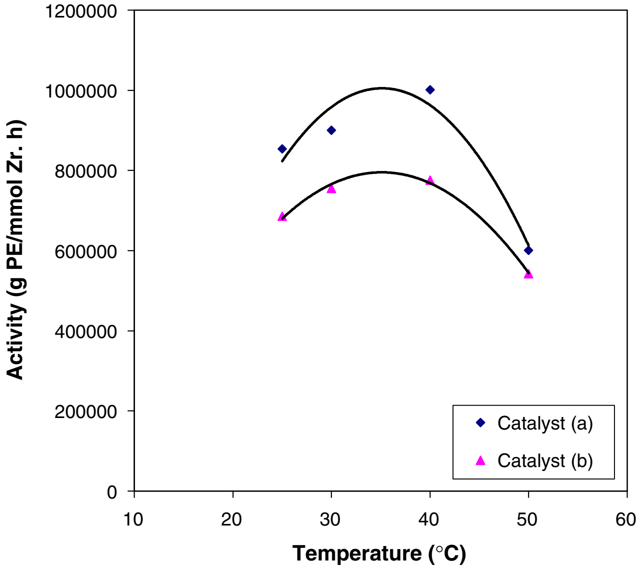


Fig. 4 Effect of temperature on the average rate of polymerization. Polymerization conditions: time=15 min, monomer pressure=2 bar, [Al]:[Zr]=80000:1, [Zr]=0.02 µmol, toluene=250 ml

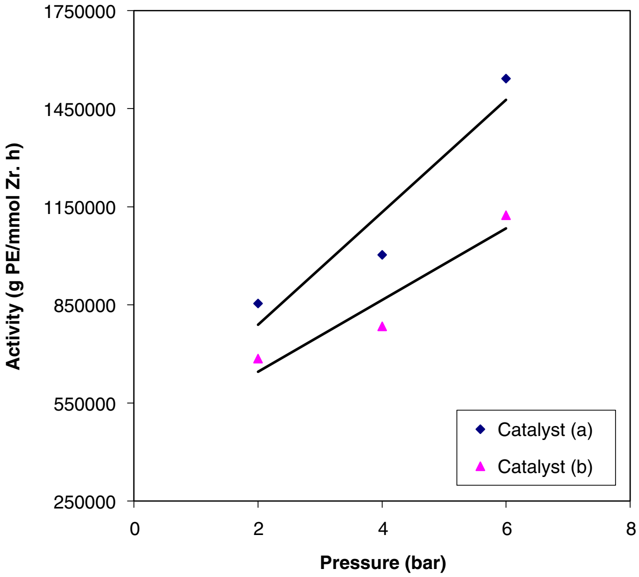


Fig. 5 Effect of monomer pressure on the polymerization behavior. Polymerization conditions as in Fig. 3

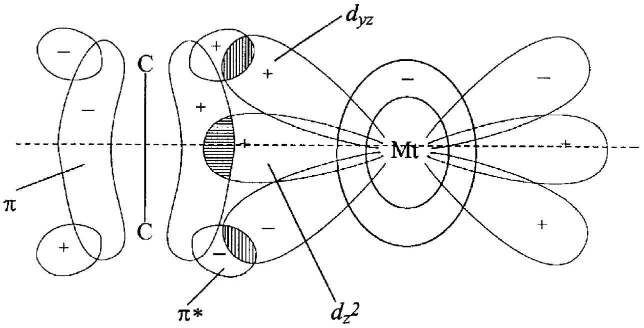


Fig. 6 Presentation of the olefin coordination on the transition metal

were carried out under dried N_2. ^1H NMR spectrum was recorded on a Bruker BRX-100 AVANCE spectrometer. Elemental analysis for CHN was carried out by CHNO type Thermo Firingan 11112EA microanalyzer.

Preparation 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. HCl (6 N, 20 ml) was added at 0°C. The organic phase was separated, dried over $MgSO_4$ and its solvent was removed, a yellow needle like solid was obtained. The yield of the reaction was about 68%. ^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).

Catalysts preparation

The procedure for the ligands and catalyst was the same as that described before in the literature [15, 16].

Bis[N-(3,5-dicumylsalicylidene)-naphthylaminato]zirconium (IV) dichloride (catalyst (a)) **Ligand** N-(3,5-dicumylsalicylidene)-naphthylamine as a gray powder. ^1H NMR ($CDCl_3$, 100 MHz): δ 1.46 (s, 9H, *t*-Bu), 2.32 (s, 3H, Me), 7.05–7.38 (m, 7H, aromatic-H), 8.59 (s, 1H, CH=N), 13.50 (s, 1H, OH). Anal. Calc. for $C_{35}H_{33}NO$: C, 86.92; H, 6.88; N, 2.90; O, 3.31. Found: C, 86.88; H, 6.95; N, 2.93; O, 3.37. **Catalyst** as a pale yellow powder. ^1H NMR ($CDCl_3$, 100 MHz): δ 1.32–1.70 (m, 18H, *t*-Bu), 2.25–2.38 (m, 6H, Me), 6.80–7.55 (m, 14H, aromatic-H), 7.91–8.13 (m, 2H, CH=N). Anal. Calc. for $C_{70}H_{64}Cl_2N_2O_2Zr$: C, 74.57; H, 5.72; N, 2.48; O, 2.84. Found: C, 74.69; H, 5.80; N, 2.44; O, 2.87.

Bis[N-(3,5-dicumylsalicylidene)-anthracylaminato]zirconium (IV) dichloride (catalyst (b)) **Ligand** N-(3,5-dicumylsalicylidene)-anthracylamine as a gray powder. ^1H NMR ($CDCl_3$, 100 MHz): δ 1.46 (s, 9H, *t*-Bu), 2.32 (s, 3H, Me), 7.05–7.38 (m, 7H, aromatic-H), 8.59 (s, 1H, CH=N), 13.50 (s, 1H, OH). Anal. Calc. for $C_{39}H_{35}NO$: C, 87.77; H, 6.61; N, 2.62; O, 3.00. Found: C, 87.89; H, 6.66; N, 2.69; O, 2.97. **Catalyst** as a pale yellow powder. ^1H NMR ($CDCl_3$, 100 MHz): δ 1.32–1.70 (m, 18H, *t*-Bu), 2.25–2.38 (m, 6H, Me), 6.80–7.55 (m, 14H, aromatic-H), 7.91–8.13 (m, 2H, CH=N). Anal. Calc. for $C_{78}H_{68}Cl_2N_2O_2Zr$: C, 76.32; H, 5.58; N, 2.28; O, 2.61. Found: C, 76.40; H, 5.65; N, 2.32; O, 2.58. Figure 1 shows Synthetic route to prepare the catalysts.

Table 1 Effect of polymerization on characteristic of the obtained polymer

Catalyst	Pressure (bar)	Temperature (°C)	H_2 (ml)	Activity (g PE/mmol Zr.h)	Crystallinity %	T_m (°C)	M_w/M_n
a	2	35	–	8.5×10^5	60	128	2.35
a	4	35	–	1.1×10^6	63	130	–
a	6	35	–	1.5×10^6	65	135	2.40
a	4	45	–	9.2×10^5	60	130	3.35
a	4	55	–	8.7×10^5	55	133	3.45
a	2	35	100	8.6×10^5	56	127	–
a	2	35	200	8.7×10^5	58	128	2.35
a	2	35	300	8.8×10^5	58	127	2.30
b	2	35	–	5.8×10^5	56	120	–
b	4	35	–	6.5×10^5	59	123	2.65
b	2	40	100	6.7×10^5	60	135	–
b	2	40	200	6.8×10^5	61	130	2.45
b	2	40	300	7.2×10^5	61	130	–

Polymerization conditions: [Al]:[Zr]=80000:1, [Zr]=0.02 μmol, Toluene=250 ml, Time=15 min

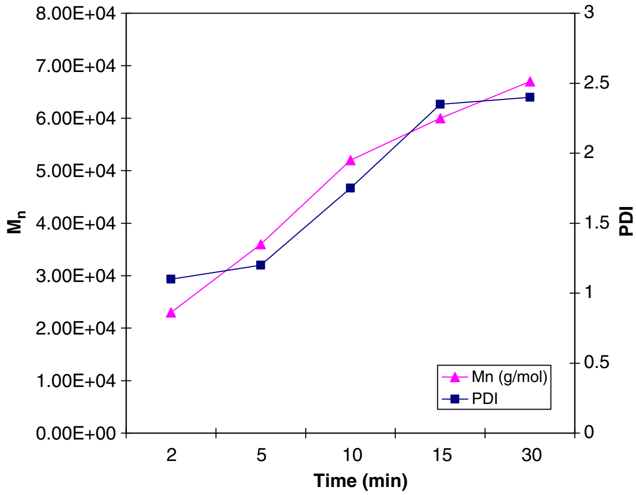


Fig. 7 PDI and M_n versus time

Result and discussion

In order to investigate the catalysts behavior, ethylene polymerization reactions were carried out at the various conditions. The activity of the catalyst, R_p (average) is expressed as g PE/(mmol Zr. h). As expected, the activity of the catalysts increased continually with the addition of the [Al]/[Zr] molar ratio (Fig. 2).

It has been reported that the steric bulk at the ortho position to the phenoxy oxygen provides steric protection toward the anionic phenoxy oxygen from coordination with lewis acidic compounds [23]. In the prepared catalysts existence of bulky cumyl group at the ortho position to the phenoxy oxygen prevents the catalysts from coordination to the cocatalyst which provides easier coordination of ethylene to the active centers resulting in increasing the activity of the catalyst to higher values [23, 24]. Using the [Al]/[Zr] molar ratio more than 120000 didn't cause any obvious further enhancement in the activity of the catalyst (b) containing anthracyl substitution. It is presumable that rigidity of the catalyst structure, sterically causes low β-hydride transfer through destabilization of β–agostic interaction, leading to survive the active sites and reduce the amount of [Al]:[Zr] molar ratio which is needed to make renew active sites. The trend of M_v values was in accordance with the mentioned presumption. The M_v values of the obtained polymer using the catalyst (b) were higher than the obtained polymer using the catalyst (a) (Fig. 3). The increase in M_v values is referred to the steric repulsion between a β-hydrogen of growing polymer and aromatic fused rings on the imine-N which could diminish β-hydride elimination through destabilization of β–agostic interaction.

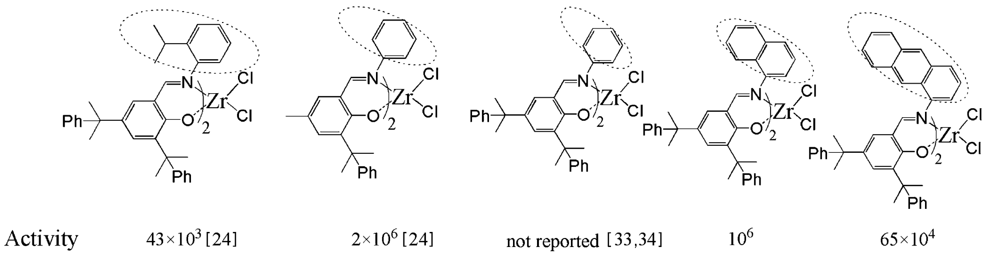
The influence of polymerization temperature on activity was investigated at the reaction temperatures between 25 and 50 °C, while the [Al]/[Zr] molar ratio was kept constant at [Al]/[Zr]=80000:1. As it can be seen in Fig. 4, the highest productivity of the catalysts was occurred at about 35–40 °C. The reduction of catalyst activity in the polymerization performed at the lower and upper temperature than the optimum value could be attributed to a low propagation rate and catalyst irreversible deactivation respectively [25]. However, higher temperature promotes easy transfer of the monomer to the catalytic active centers as well as reducing the solubility of the monomer gas in the polymerization medium [25, 26].

The influence of monomer pressure between 2 and 6 bars on the catalyst behavior was studied. The polymerization behavior is shown in Fig. 5. The higher the pressure of the monomer, the higher the activity of the catalysts was observed. The behavior is mainly due to high concentration of the monomer close to the catalyst active centers [3, 20, 25].

Although the increase of the monomer pressure enhanced the M_v value of the obtained polymer using both catalysts, catalyst (b) was more sensitive to the monomer pressure and as it can be seen in Fig. 3, M_v values of the resulting polymer were increased dramatically.

Among catalyst components, ligand plays a predominate role in polymerization process. During electron exchange between metal and monomer, ligand aids metal to balance its electron density with receiving electrons from the coordinated ethylene through metal and releasing electrons whenever required to facilitate ethylene insertion process (Fig. 6) [27]. Generally, active ligands possess well-balanced electron-donating and electron-withdrawing properties and therefore have a small energy gap between HOMO and LUMO [28, 29]. Presumably the steric effect due to overwhelming steric congestion derived from the fused aromatic substitutions more than electronic effect could affect the catalyst activity.

Fig. 8 Influence of different substitutions on the catalyst activity under similar polymerization conditions



Ethylene polymerization was carried out using different amount of hydrogen as a chain transfer agent. As it can be seen in Table 1, higher amount of hydrogen could increase the activity of the catalysts. A reasonable explanation for this effect might be the more homogeneous reaction conditions, but a fast hydrogenation of less reactive intermediates such as those resulting from 2,1-insertions is also conceivable [30].

The molecular weight distribution of some polyethylene samples was determined using the GPC method. The results are summarized in Table 1. According to the Table, the obtained polyethylene has a melting point of about 120–135 °C and crystallinity of about 55–65%. Higher pressure increased both the crystallinity and the M_v values of the resulting polymer (Table 1).

As it is shown in Fig. 7, polydispersity remarkably increases with time which reveals that the system starts to deviate from pure living behavior. The reason can be that either the catalyst is not truly living over the full polymerization time or that the single-site system turns into a multi-site system due to heterogenization of the system. This would strongly influence diffusion of ethylene to the living active centers. This phenomenon could be comparable with self-immobilization of single-site catalysts that has been a subject of interest recently [31]. Similar result has been reported already by Ivanchev et. al [32]. The capture and blocking of active sites by the grown polymer after a certain polymerization time have been suggested.

For short reaction times, a linear dependence between the polymerization time and the molar weight was observed indicating for living behavior. Due to the fast polymerization rate as well as rapid precipitation of the obtained polymer which leads to heterogenization of the catalyst system, the PDI can be broadened by time.

To make a comparison between the activity of the prepared catalysts and those reported already, we compared the activities of some well-known FI Zr-based catalysts with the data reported in this study. According to the results collected in Fig. 8, plurality of the fused aromatic rings on the N atom of the imine moiety in the catalyst structure has influenced the polymerization activity as well as the molecular weight of the resulting polymer (Table 1).

Although, replacement of anilinato-group with naphtylaminato or anthracylaminato-group provides spatial difficulties in accessibility of the active centers which results in decreasing the activity, it leads to an increase in the molecular weight of the resulting polymer. The results reveal that only the electronically flexibility of the ligand is not a necessity to reach high activities of the catalysts, but an appropriate integration of catalyst electronic properties as well as catalyst steric characteristics is required.

Conclusion

Changing of ligand from FI-type single aryl substituted on the N atom of imine to further aromatic fused rings enhanced the steric hindrance of the catalyst which resulted in diminishing the catalyst activity in comparison with FI catalysts including single aryl substituted on the N. However, this replacement could increase the molecular weight of the polymer obtained. Polymerization activity was increased with the increasing of both the monomer pressure and [MAO]/[Zr] molar ratio. Higher ethylene pressure increased the activity of the catalysts with the same trend and increased the crystallinity as well as the M_v values of the resulted polymer. Crystallinity and melting point of the obtained polymer were between 55–65% and 120–135°C respectively. Although a linear dependence between the polymerization time and the molar weight was observed indicating for living behavior, but the polydispersity was broadened with the time.

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