

Comparative Ethylene Polymerization via Imino-Quinolinol Catalysts¹

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Abstract—A series of zirconium catalysts based on tridentate 8-hydroxyquinoline Schiff base ligands were prepared and successfully used for polymerization of ethylene. The highest activities of the prepared catalysts were obtained at polymerization temperatures about 30–45°C. By increasing the [Al]/[Zr] molar ratio productivity of all the catalysts enhanced to an maximum value then decrease at higher [Al]/[Zr] molar ratio with the exception of catalyst **4**, which showed no optimum activity in the range studied. Also, the activities and selectivities to produce low-carbon olefins were profoundly influenced by the catalysts structure indicating the dramatic effects of the substitution on the polymerizations behavior. Fouling of the reactor was strongly related to polymerization parameters like as monomer pressure and [Al]/[Zr] ratio in the homogeneous polymerization. Heterogeneous polymerization of ethylene using the catalysts and the MAO modified silica decreased the fouling. The obtained polyethylenes have a melting point of about 125–130°C, crystallinities of about 45–55% and PDI of 2.45–3.45.

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INTRODUCTION

8-Hydroxyquinoline is a high consumption ligand in coordination chemistry [1], which is useful for many purposes. It has been reported that the Ti, Zr, and Hf complexes with the heteroatom chelating ligands such as hydroxyquinolines and hydroxypyridines complexes show a catalytic activity on dehydrogenation [2]. The group 4 transition metals are capable to complex the groups such as cyclopentadienyl-based, phenoxy imine, phenoxy pyridine, phenoxy ether, pyrrolide imine, indolide imine, imine pyridine or phenoxy imine pyridine chelate ligands resulted in the introduction of numerous metallocene and non-metallocene systems [3–9].

In recent years the advent of new class of group four transition metal catalysts bearing *O,N*-chelating ligands so called FI catalysts by Fujita and coworkers [10–12] and a series of Ni and Pd based α -diimine catalysts by Gibson [13, 14], Brookhart [15, 16] and Chen for ethylene polymerization and oligomerization have inaugurated substantial revolution in the field of olefin polymerization [17–22].

As mentioned above, zirconium(IV) chloride complexes which contain substituted bis(8-quinoline) and bis(oxazoline) [23, 24] chelating ligands are confined in organic chemical reactions such as palladium-catalyzed allylic coupling and Diels-Alder reactions and less attention has been devoted to the polymerization using the same complexes. However, Bei, Swenson and Jordan reported ethylene polymerization reactivity of 8-quinolato ligands [25]. Also olefins polymerization reactivity of the catalysts based on Schiff bases derivatives of 8-hydroxyquinoline-2-carboxaldehyde has been described [26]. Moreover, Hu et al., studied synthesis and ethylene polymerization of a series of half-sandwich zirconium complexes bearing imino-quinolinol and Cp ligands [27]. However, less attention has been paid to the catalytic behavior during the polymerization using such catalysts.

In continuation of research on design and synthesis of organometallic catalysts and their application in olefin polymerization [28–31], in the present study, a series of zirconium(II) catalysts containing 8-quinolato with *N,N,O*-chelating ligand has been synthesized and used in ethylene polymerization.

¹ The article is published in the original.

EXPERIMENTAL

Materials and Instruments

Methylene chloride, methanol, para-toluenesulfonic acid, zirconium(IV) chloride and amine derivatives were purchased from Merck Chemical (Darmstadt, Germany). Toluene and *n*-hexane was supplied by Arak Petrochemical Co (Arak, Iran), the chemicals were purified by distillation over sodium wire, stored over 13X and 4A activated molecular sieves. 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) and triisobutylaluminum (TIBA) (purity 93%) was supplied by Sigma Aldrich Chemicals (Germany).

Differential scanning calorimetry (DSC) (Mettler Toledo DSC822) with a rate of heating 10 grad/min was used for characterization of the degree of crystallinity of PE according to known procedure using the heat of fusion of pure crystalline PE equal to 288 cal/g [32, 33].

The viscosity average molecular weight M_v was determined by viscometry in decaline at 135°C using an Ubbelohde viscometer and calculated through Mark–Houwink equation $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$. The molecular weight and the molecular weight distribution were analyzed by gel permeation chromatography (GPC) (Waters, Milford, MA 2000) instruments at 135°C and trichlorobenzene was used as a solvent. Polystyrene narrow dispersed standards were used for calibration.

¹H NMR spectra were recorded with a BRUKER DRX AVANCE spectrometer at 298 K and 100 MHz. C₄–C₁₀ olefins were determined by GC system QP 2010-plus Shimadzu. The percent of compound higher than C₁₀ were measured by calculation of the rest of products.

Ethylene Polymerization

MAO/SiO₂ (MAO modified silica) was prepared according to the literature [34, 35]. All the catalyst preparation and polymerization procedure were carried out under dried argon atmosphere in 1-L stainless steel Buchi reactor (bcp 250) equipped with controllers systems as described before [28]. Toluene (300 mL) was introduced into the argon-purged reactor and stirred (350 rpm) and the reactor was kept at the suitable temperature. TIBA was used as scavenger and was added to the reactor prior to addition of the MAO. MAO and the catalyst were charged into the reactor under a positive pressure of ethylene via syringe respectively. Ethylene gas feed was started and the pressure of reactor was kept stable. After 10 min, the gas feed shut off and reaction was terminated by

addition of methanol containing 5 wt % HCl. The polymer was precipitated and dried at 60°C for 24 h.

Ligand Preparation

Synthesis of 8-hydroxy-2-[*N*-(phenylimino)methyl]-quinoline (L1). To a solution of aniline (1.1 equiv.) in ethanol (20 mL), 8-hydroxy-2-quinolinecarboxaldehyde (1 equiv.) and a trace amount of para-toluenesulfonic acid were added. The obtained yellow solution was refluxed for 4 h. The solvent was removed and the obtained yellow solid was washed with *n*-hexane and dried. The ligand was obtained as orange solid with a yield of 88%. ¹H NMR (100 MHz, CDCl₃), δ_H, ppm: 7.25–7.45(m, 3H), 7.50–7.84 (m, 4H), 7.90 (m, 1H), 8.22 (broad s, 1H, OH), 8.35–8.50 (m, 2H), 8.80 (s, 1H, CH=N).

Synthesis of 8-hydroxy-2-[*N*-(1-naphtylimino)methyl]-quinoline (L2). The procedure was the same as that described above. The ligand was obtained as orange solid with a yield of 87%. ¹H NMR (100 MHz, CDCl₃), δ_H, ppm: 7.15–7.40 (m, 4H), 7.50–7.85 (m, 6H), 7.90 (m, 1H), 8.20 (broad s, 1H, OH), 8.32 (d, 1H, *J* = 8.6 Hz), 8.90 (s, 1H, CH=N).

Synthesis of 8-hydroxy-2-[*N*-(2,4,6-trimethylphenylimino)methyl]-quinoline (L3). The procedure was the same as that described for above ligand. The ligand was obtained as yellow crystals with a yield of 77%. ¹H NMR (100 MHz, CDCl₃), δ_H, ppm: 2.20–2.30 (m, 9H), 6.90–7.55 (m, 7H), 8.32 (broad s, 1H, OH), 8.55 (s, 1H, CH=N).

Synthesis of 8-hydroxy-2-[*N*-(2,6-diisopropylphenylimino)methyl]-quinoline (L4). The procedure was the same as that described before. The ligand was obtained as yellow crystals with a yield of 73%. ¹H NMR (100 MHz, CDCl₃), δ_H, ppm: 1.25 (d, 12H), 3.2 (m, 2H), 7.28–7.58 (m, 8H), 8.3 (broad s, 1H, OH), 8.45 (s, 1H, CH=N).

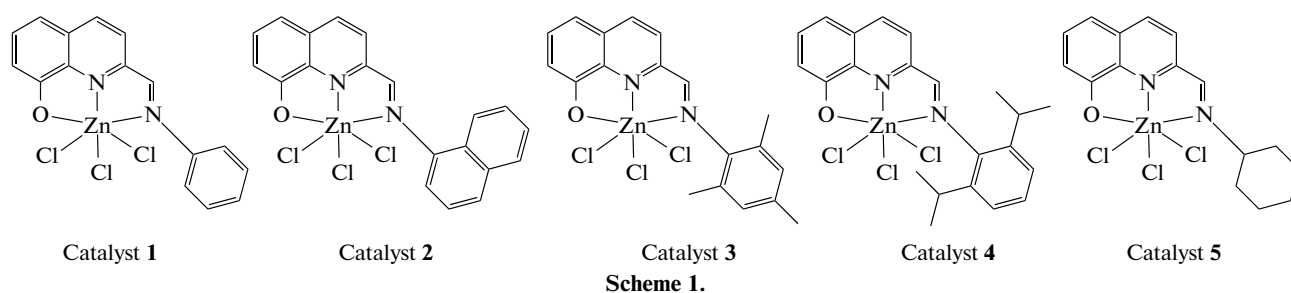
Synthesis of 8-hydroxy-2-[*N*-(cyclohexylimino)methyl]-quinoline (L5). The procedure was the same as that described before. The ligand was obtained as orange solid with a yield of 84%. ¹H NMR (100MHz, CDCl₃), δ_H, ppm: 1.40–1.85 (m, 10H), 3.40 (m, 1H, CH cyclohexyl), 7.19–7.34 (m, 5H), 8.15 (broad s, 1H, OH), 8.75 (s, 1H, CH=N).

Catalyst Preparation

To a stirred solution of 8-hydroxy-2-[*N*-(phenylimino)methyl]-quinoline (2.5 mmol) (L1) in THF (20 mL) at –78°C, *n*-BuLi (2.8 mmol, 1.6 M in hexane) was added drop wise. The orange solution was warmed to room temperature and stirred for 4 h. To the resulting solution a suspension of ZrCl₄ (2.5 mmol in THF) was added slowly. The resulting mixture was then warmed to room temperature and stirred for 24 h. After removing the solvent, the complex was extracted

with 20 mL of dry dichloromethane. The filtrate was evaporated and the residue was washed twice with dry *n*-hexane. The resulting solid was dried under N₂ to obtain the catalyst **1** as dark red powder (82% yield).

Complexes **2** to **5** were obtained from ligands L2 to L5 following the same procedure as that used for obtaining complex **1** from ligand L1. Scheme 1 showed the structure of the prepared catalysts.



Complex 1. Anal. calcd. for C₁₆H₁₁Cl₃N₂OZr, %: C, 43.20; H, 2.49; N, 6.30; O, 3.60; Found, %: C 43.08; H 2.44; N, 6.22; O, 3.56. Mass: *m/z*, 441 [M]⁺.

Complex 2. Anal. calcd. for C₂₀H₁₃Cl₃N₂OZr, %: C, 48.54; H, 2.65; N, 5.66; O, 3.23; Found, %: C 48.43; H 2.62; N, 5.60; O, 3.21. Mass: *m/z*, 491 [M]⁺.

Complex 3. Anal. calcd. for C₂₀H₁₈Cl₃NOZr, %: C, 49.43; H, 3.73; N, 2.88; O, 3.29; Found, %: C, 49.37; H, 3.70; N, 2.83; O, 3.26. Mass: *m/z*, 483 [M]⁺.

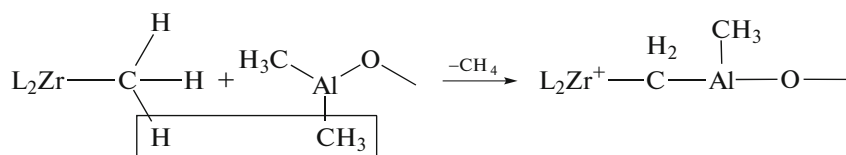
Complex 4. Anal. calcd. for C₂₂H₂₃Cl₃N₂OZr, %: C, 49.95; H, 4.38; N, 5.30; O, 3.02; Found, %: C, 49.85; H, 4.33; N, 5.27; O, 2.99; Mass: *m/z*, 526 [M]⁺.

Complex 5. Anal. calcd. for C₁₇H₁₈Cl₃NOZr, %: C, 45.38; H, 4.03; N, 3.11; O, 3.56; Found, %: C, 45.25; H, 3.99; N, 3.06; O, 3.51. Mass: *m/z*, 447 [M]⁺.

RESULTS AND DISCUSSION

Ethylene polymerization was carried out using the prepared catalysts in toluene. The catalysts activity is

defined as g(PE)/(mmol Zr h), it was determined after 10 min. The catalysts activities were increased with the [Al]/[Zr] ratios to a maximum value, beyond this ratio catalyst activities decrease with the exception of catalyst **4** which increased linearly in the range studied (Fig. 1). This behavior may be due to extreme complexation of MAO with the active centers that made active centers unavailable for the monomer insertion and decreased the catalysts activities [36]. Additionally, introducing of bulky isopropyl substitutions in the catalyst structure might protect the catalyst from coordination to the co catalyst resulting in a linear increase of activity against increasing the [Al]/[Zr] molar ratio. Moreover, Chen and Marks [37], reported that an important deactivation process for MAO activated catalytic systems is α -hydrogen transfer which leads to the production of methane and catalytically inactive Zr-CH₂-Al or Zr-CH₂-Zr species (Scheme 2).



The polymerization of ethylene was carried out at temperature range from 20 to 50°C at [Al]/[Zr] = 3000/1 molar ratio (Fig. 2). The catalysts **1** and **3** showed the highest activity in the polymerization at 30°C. However, the catalysts **2**, **4** and **5** showed the highest productivity at about 35–40°C. Among the zirconium catalysts, catalyst **4** containing sterically bulky substitutions exhibited the lowest polymerization activity. Among the synthesized catalysts, catalyst **5** bears the electronically most donation ligand, which stabilized the metal catalyst even at high polymerization temperature. In the other words, thermal stability

of metal catalyst was improved by the surrounding of the metal catalyst with high electron efficient ligands.

The results showed that both catalytic activity and selectivity to produce low-carbon olefins under the same polymerization conditions are attributed to the steric congestion on the catalyst and the flexibility of the ligand in coordination structure. As it can be seen in Table 1, the catalyst **5** exhibited the highest activity and the lowest selectivity to low-carbon olefins. It was observed that the catalysts **1** and **5** have higher activities than their analogues.

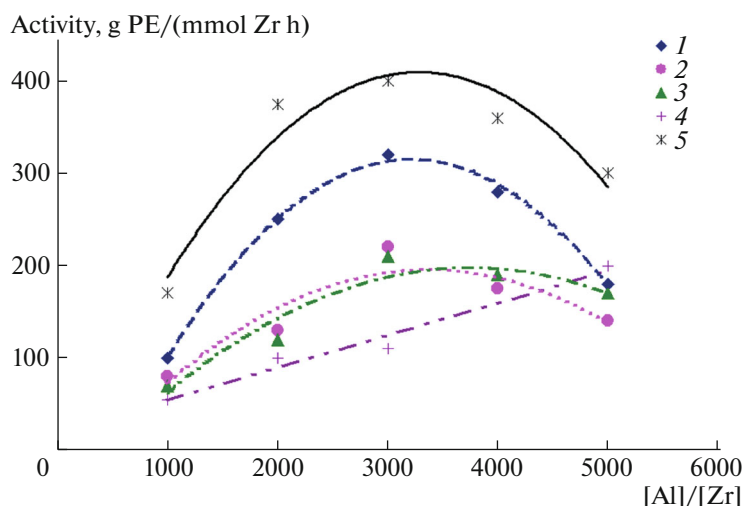


Fig. 1. (Color online) Effect of $[Al]/[Zr]$ ratio on the activities of catalysts (1) 1, (2) 2, (3) 3, (4) 4, and (5) 5. Polymerization conditions: 35°C, 15 min, pressure 3 bar, $[Zr] = 0.018$ mmol.

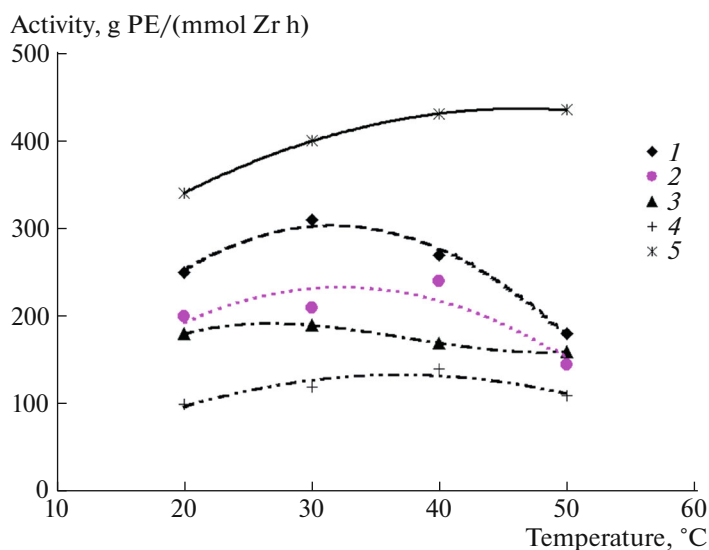


Fig. 2. (Color online) Effect of polymerization temperature on the activities of catalysts (1) 1, (2) 2, (3) 3, (4) 4, and (5) 5. Polymerization conditions: 10 min, pressure 3 bar, $[Al]/[Zr] = 3000/1$, $[Zr] = 0.018$ mmol.

The effect of monomer pressure on the catalysts activities was studied. The increasing of the monomer pressure enhanced the activities of the catalysts, the degree of crystallinity as well as M_v values. The molecular weight distribution of some polyethylene samples was determined using GPC. The results are summarized in Table 1. The obtained PEs showed a melting point at about 125–130°C, crystallinity of about 45–55% and PDI of 2.45–3.45. Furthermore, M_v values of the resulting polyethylene were between 1.05×10^4 and 1.95×10^4 at the identical conditions.

It was observed that electronic characteristic of the ligands make discrepancy in metal catalyst response to

the polymerization condition [17–22, 39, 40]. Usually, homogeneous olefin polymerization catalysts occurs if the metal exists in high oxidation state, as a consequence, stabilization of the intermediate catalyst-olefin adduct by back bonding is not possible. Stronger the electron donating ligand, more stable will be the metal in high oxidation state in a metal catalyst. It was observed that ligand-induced rigidity by ligand bulky substitution enhance polymer molecular weight. In our previous studies, we reported that destabilization of beta-agostic interaction in olefin-catalyst intermediate is responsible to produce high molecular weight polymer [38]. The same mechanistic explanations have been also reported in literature [18–22, 39].

Table 1. Some specification of the resulting polymers

Cat.	Pressure, bar	Temp., °C	Activity $\times 10^{-2}$, gPE/(mmol Zr h)	C4, %	C10, %	> C10, %	T_m , °C	Crystallinity, %	$M_v \times 10^{-4}$, g/mol	M_w/M_n
1	3	35	3.2	9	19	72	130	48	1.45	2.45
2	3	35	2.3	38	49	13	126	45	1.05	2.80
3	3	35	2.2	11	22	67	128	55	1.85	3.10
4	3	35	1.3	26	33	41	126	45	1.71	2.24
5	3	35	4.1	8	18	74	125	49	1.92	3.45
1	3	50	2.4	—	—	—	127	47	—	—
1	5	35	3.9	—	—	—	130	48	—	—
5	5	35	4.8	6	11	83	125	55	2.10	—
5	7	35	5.8	4	8	82	128	55	2.35	—

Polymerization conditions: 10 min, [Al]/[Zr] = 3000/1, [Zr] = 0.018 mmol, Toluene 250 mL.

However, it can be concluded that in the case of catalyst **5** the both steric and electronic nature of cyclohexyl imino moiety affected the polymer molecular weight in different mechanism.

Fouling was observed in polymerization reactor due to catalysts structures. Heterogeneous polymer-

ization using the catalysts and the MAO/SiO₂ (MAO modified silica) employing the same polymerization condition improved morphology of the polymer particles (Fig. 3). Elimination of the dusty particles due to the heterogeneous polymerization decreased the fouling of the reactor. Although the fouling of reactor

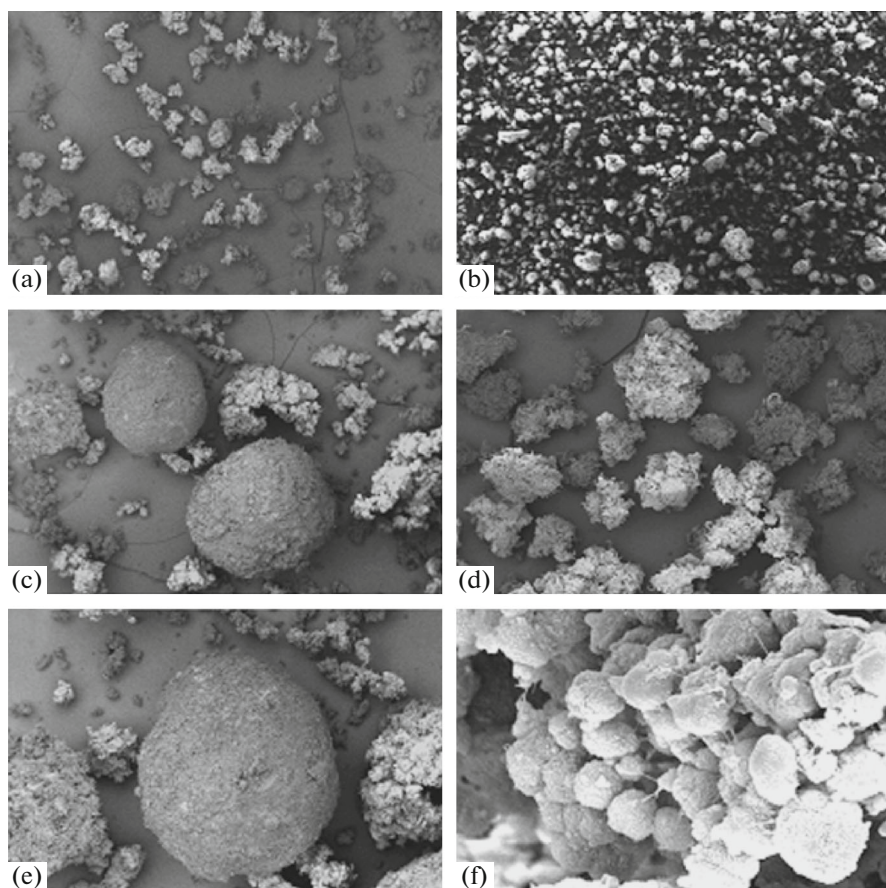


Fig. 3. SEM micrographs of the polyethylenes obtained using (a), (b) homogeneous and (c), (d), (e), (f) heterogeneous form of catalyst **5**, magnification: (a), (b) 100 \times , (c), (d) 250 \times , (e) 1000 \times , and (f) 10000 \times .

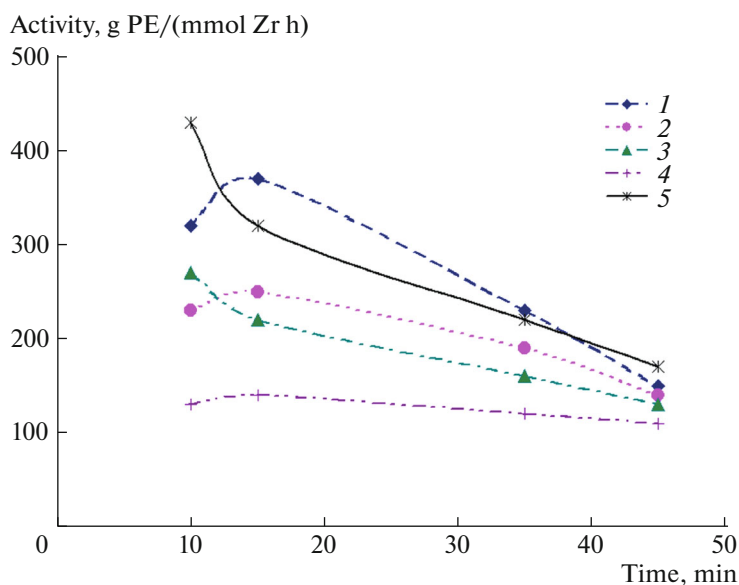


Fig. 4. (Color online) Catalysts activities versus polymerization time of catalysts (1) **1**, (2) **2**, (3) **3**, (4) **4**, and (5) **5**. Polymerization conditions: pressure 3 bar, $[Al]/[Zr] = 3000/1$, $[Zr] = 0.018$ mmol, at optimum temperature for each catalyst according to Fig. 3.

removed using the supported catalyst, the catalyst activity was diminished.

The dependence between catalyst activity and polymerization time was also investigated as it is a substantial factor in this scope. Therefore, ethylene polymerization was carried out with prolonged reaction time (up to 45 min) in order to ascertain the lifetime of the catalyst. As it can be seen in Fig. 4, the reaction time can have a significant effect on activity. For the catalysts **1** and **2**, as reaction time increases, the activity increased and after reaching a maximum, it decreases. These maximums for the catalysts **1** and **2** are 15 min. However, catalyst activity for the catalysts **3** and **5** were continually diminished as and the polymerization time increased. Negligible activity of the catalyst **4** remains nearly constant after 45 min of the polymerization.

CONCLUSIONS

Five catalyst based on 8-quinolinato with *N,N,O*-chelating ligand were prepared and used in ethylene polymerization. The steric hindrance caused by the bulky (2,6-diisopropylphenylimino) substitutions on the catalyst **4** prevents proper interaction between the zirconium atom and the π -electron of the ethylene monomer leading to a deceleration of chain propagation in ethylene polymerization. However, it apparently results in increasing the selectivity to produce oligomerized ethylene. In the case of catalyst **2** with (1-naphtylimino) substitution of fused aromatic rings on the catalyst structure, increased the rigidity of the catalyst leading to decrease the activity in comparison with the catalyst **1** with (phenylimino) substitutions.

However, it enhanced the tendency of the catalyst to produce low-carbon olefins. The monomer pressure and $[MAO]/[Zr]$ ratio increased catalysts activities, whereas fouling of the reactor increased. However, heterogeneous polymerization improved morphology of the resulting polymer and decreased fouling of the polymerization reactor. Melting point of about 125–130°C, crystallinity of about 45–55% and PDI of 2.45–3.45 were obtained from polyethylenes afforded by the catalysts.

REFERENCES

1. C. Bakewell, G. Fateh-Iravani, D. W. Beh, D. Myers, S. Tabthong, P. Hormnirun, A. J. P. White, N. Long, and C. K. Williams, *Dalton Trans.* **44**, 12326 (2015).
2. S. Taubmann and H. Alt, *J. Mol. Catal. A: Chem.* **289**, 49 (2008).
3. Y. Nakayama, H. Bando, Y. Sonabe, and T. Fujita, *J. Mol. Catal. A: Chem.* **213**, 141 (2004).
4. Y. Yoshida, S. Matsui, and T. Fujita, *J. Organomet. Chem.* **690**, 4382 (2005).
5. C. Cobzara, S. Hilds, and A. Boger, *Coord. Chem. Rev.* **250**, 189 (2006).
6. H. Makio, H. Terao, A. Iwashita, and T. Fujita, *Chem. Rev.* **111**, 2363 (2011).
7. S. Damavandi, S. Ahmadjo, R. Sandaroods, and G. H. Zohuri, in *FI Catalyst for Polymerization of Olefin, in Polymerization*, Ed. by A. De Souza Gomes, (InTech, Rijeka, 2012).
8. S. Damavandi, R. Sandaroods, and M. A. Shamekhi, *J. Macromol. Sci., Part A: Pure. Appl. Chem.* **49**, 339 (2012).
9. K. Osakada, *Organomet. React. Polym.* **85**, 89 (2014).
10. S. Matsui and T. Fujita, *Catal. Today* **66**, 63 (2001).

11. Y. Suzuki, H. Terao, and T. Fujita, *Bull. Chem. Soc. Jpn.* **76**, 1493 (2003).
12. H. Makio, H. Terao, A. Iwashita, and T. Fajita, *Chem. Rev.* **111**, 2363 (2011).
13. G. J. P. Britovsek, V. C. Gibson, and D. F. Wass, *Angew. Chem., Int. Ed. Engl.* **38**, 428 (1999).
14. G. J. P. Britovsek, V. C. Gibson, and B. S. Kimberley, *Dalton Trans.* **2001**, 1639 (2001).
15. S. A. Svejda and M. Brookhart, *Organometallics* **18**, 65 (1999).
16. C. M. Killian, L. K. Johnson, and M. Brookhart, *Organometallics* **16**, 2005 (1997).
17. L. Guo, S. Dai, X. Sui, and C. Chen, *ACS. Catal.* **6**, 428 (2016).
18. L. Guo and C. Chen, *Sci. China: Chem.* **58**, 1663 (2015).
19. S. Dai, X. Sui, and C. Chen, *Angew. Chem., Int. Ed.* **54**, 9948 (2015).
20. S. Dai and C. Chen, *Angew. Chem., Int. Ed.* **55**, 13281 (2016).
21. W. Zou and C. Chen, *Organometallics* **35**, 1794 (2016).
22. R. Wang, X. Sui, W. Pang, and C. Chen, *ChemCatChem* **8**, 434 (2016).
23. P. G. Cozzi and C. Floriani, *Inorg. Chem.* **34**, 2921 (1995).
24. P. G. Cozzi, E. Gallo, and C. Floriani, *Inorg. Chem.* **14**, 4994 (1995).
25. X. Bei, D. C. Swenson, and R. F. Jordan, *Organometallics* **16**, 3282 (1997).
26. C. L. Hillairet, G. Michaud, and S. Sirol, US Patent No. 20100004411 A1 (2010).
27. P. Hu, F. Wang, and G. X. Jin, *Organometallics* **30**, 1008 (2011).
28. S. Damavandi, G. H. Zohuri, R. Sandaroos, and S. Ahmadjo, *J. Polym. Res.* **19**, 9796 (2012).
29. W. Yang, T. Taniike, M. Terano, Y. Chen, and W. H. Sun, *J. Braz. Chem. Soc.* **12**, 2244 (2014).
30. R. Sandaroos, S. Damavandi, and A. Farhadipour, *Macromol. Chem. Phys.* **211**, 2339 (2010).
31. M. Khoshsefat, G. H. Zohuri, N. Ramezani, S. Ahmadjo, and M. Haghpanah, *J. Polym. Sci., Part A: Polym. Chem.* **54**, 3000 (2016).
32. A. Peacock, *Handbook of Polyethylene: Structures: Properties, and Applications* (Marcel Dekker Inc., New York, 2000).
33. S. Damavandi, N. Samadieh, S. Ahmadjo, Z. Etamadnia, and G. H. Zohuri, *Eur. Polym. J.* **64**, 118 (2015).
34. A. Talaei, F. Afshar Taromi, A. Arefazar, S. Ahmadjo, and O. Moini Jazani, *Chin. J. Polym. Sci.* **32**, 137 (2014).
35. M. M. Mortazavi, S. Ahmadjo, J. H. Z. Dos Santos, H. Arabi, M. Nekoomanesh, G. H. Zohuri, R. Brambilla, and G. B. Galland, *J. Appl. Polym. Sci.* **130**, 4568 (2013).
36. M. Khoshsefat, N. Beheshti, G. H. Zohuri, S. Ahmadjo, and S. Soleimanzadegan, *Polym. Sci., Ser. B* **58**, 487 (2016).
37. E. Y. X. Chen and T. J. Marks, *Chem. Rev.* **100**, 1391 (2000).
38. S. Ahmadjo, G. H. Zohuri, S. Damavandi, and R. Sandaroos, *React. Kinet., Mech. Catal.* **101**, 429 (2010).
39. H. Mu, L. Pan, D. Song, and Y. Li, *Chem. Rev.* **115**, 12091 (2015).
40. R. Wang, M. Zhao, and C. Chen, *Polym. Chem.* **7**, 3933 (2016).