

*Synthesis and application of fluorinated
 α -diimine nickel catalyst for ethylene
polymerization: deactivation mechanism*

**S. Ahmadjo, S. Damavandi,
G. H. Zohuri, A. Farhadipour,
N. Samadieh & Z. Etemadinia**

Polymer Bulletin

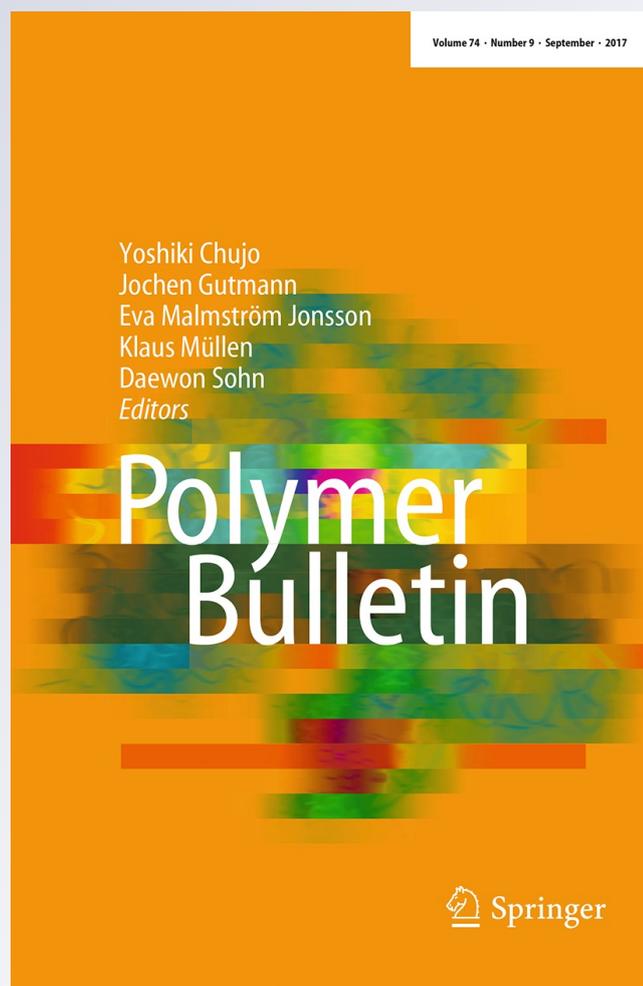
ISSN 0170-0839

Volume 74

Number 9

Polym. Bull. (2017) 74:3819-3832

DOI 10.1007/s00289-017-1924-3



Your article is protected by copyright and all rights are held exclusively by Springer-Verlag Berlin Heidelberg. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



Synthesis and application of fluorinated α -diimine nickel catalyst for ethylene polymerization: deactivation mechanism

S. Ahmadjo¹ · S. Damavandi² · G. H. Zohuri² ·
A. Farhadipour² · N. Samadieh² · Z. Etemadinia²

Received: 19 July 2016 / Revised: 6 December 2016 / Accepted: 23 January 2017 /
Published online: 3 February 2017
© Springer-Verlag Berlin Heidelberg 2017

Abstract A fluorinated LTM catalyst of [bis(*N,N'*-2-fluorophenylimino)acenaphthene] nickel(II) dibromide was prepared and applied for ethylene polymerization. We established a reasonable hypothesis, highlighting the role of fluorine in ligand structure. In addition, density functional theory (DFT) studies have been applied to strengthen our propositions. DFT calculations of the β -agostic cationic species at room temperature and 75 °C suggest that the β -agostic structure for the latter was destabilized by 19 eV which rendered it less prone to β -H transfer reactions than the species at room temperature. In addition, a mechanism for the catalyst deactivation for fluorinated α -diimine nickel based catalysts has been proposed.

Keywords Late transition metal · α -Diimine · Nickel catalyst · DFT · Deactivation mechanism

Introduction

Since the development of the first Ziegler–Natta (1953–1954) and Phillips catalysts (late 1940s), there has been a significant drive to increase catalytic activity, increase the control of polymer structure and comonomer content, and at the same time reduce the cost of the polymerization system [1–4]. The development of the metallocene catalyst systems has allowed for increased control of polymer structure

✉ S. Ahmadjo
s.ahmadjo@ippi.ac.ir

✉ G. H. Zohuri
Zohuri@um.ac.ir

¹ Department of Catalyst, Iran Polymer and Petrochemical Institute, Tehran, Iran

² Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

and molecular weight distribution, resulting in highly stereospecific systems and systems which can produce polymers with novel properties [5–7].

The discovery of α -diimine derived late transition metal (LTM) catalysts has led to a surge in interest in olefin polymerizations by catalysts other than those derived from the more traditional, early metal complexes [8]. These catalysts allow unprecedented ethylene and α -olefin homo- and copolymerization with a variety of other monomers [8, 9]. This resulted in the development of several generations of late-transition metal catalysts. Initial work with these systems was focused on the modification of the nickel-based shell higher olefins process (SHOP) oligomerization catalysts, it was discovered by Keim and Mecking [10, 11], that the catalysts could be modified via the introduction of steric bulk to the ligand, to produce higher molecular weight materials [12]. Subsequent variations to the ligand structure resulted in higher molecular weight materials, and eventually very good stereo control of the polymers [13–15]. Perhaps the most recognized and successful of these variations are the Brookhart diimine catalysts [16, 17]. These systems produce high molecular weight materials with high activities by controlling the chain termination and transfer rates using the pseudo-axial bulk of the ligand [16–18]. This understanding of the function of pseudo-axial bulk led to the development of other catalyst systems such as the Grubbs salicylaldimine [19]. Afterward, tremendous efforts have been spent in both industrial and academic laboratories on improving LTM Brookhart's catalyst systems. Many structural modifications, including steric tuning, changing the ligand backbone structure, and changing the chelating heteroatoms, have been pursued on the archetype α -diimine ligands [20, 21]. Brookhart and coworkers observed an increase in polar olefin incorporation for increasingly electron-donating ligands [22]. Moreover, Guan and his coworker investigated electronic effects of substitutions for a range of Pd based α -diimine catalysts for ethylene polymerization [23]. They reported that the ligand electronic structure of the catalysts has a significant effect on topology of the polyethylene formed as well as catalyst activity. Furthermore, Alt and coworkers studied the electronic influence of the ligand structure on the catalytic properties of α -diimine nickel catalysts in the polymerization and oligomerization of ethylene by incorporating halogen substituent at the different positions of the arene moieties of the ligand [24].

As a part of our ongoing research in synthesis and application of polyolefin catalysts, [25–27] herein, we wish to describe the synthesis and ethylene polymerization of [bis(N,N' -2-fluorophenylimino)acenaphthene] nickel (II) dibromide catalyst. The details of polymerization as well as polymer characterization have been also described.

Experimental

Materials

Dichloromethane, diethyl ether, methanol, *p*-TsOH and 2-fluoro aniline were supplied by Merck Chemical (Darmstadt, Germany) and were used as received.

Toluene and *n*-hexane were obtained by Arak Petrochemical Co (Arak, Iran). The chemicals were prepared from distilling over CaH₂, sodium wire and benzophenon, respectively. The distilled chemical was stored over 13X and 4A type 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). The gases were purified as explained in the literature [25]. Methylaluminoxane (MAO) (10% solution in toluene), triisobutylaluminum (TIBA) (purity 93%), acenaphthoquinone (purity >99%) and (DME)NiBr₂ were purchased from Sigma Aldrich chemicals (Steinheim, Germany).

Ethylene polymerization

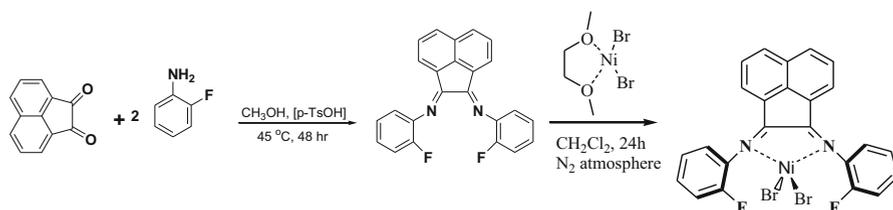
The polymerization was performed in a stainless steel Buchi reactor size 1 L equipped with an agitator. The reactor was evacuated and purged with N₂ several times at 110 °C for removing of oxygen and moisture. Toluene was added into the reactor at room temperature and saturated with ethylene gas. TIBA was used as scavenger and added to the reactor before addition of the MAO. Following to, various MAO and catalyst ratio were added, respectively, with stirring at 800 rpm under specific ethylene pressure. Ethylene gas feed was started and the pressure of reactor was kept constant at the applied monomer pressure for each run. After finishing the polymerization, the residue ethylene gas was released out of reactor and the polymer slurry was quenched with acidic ethanol. The polymer was filtrated, washed with ethanol and dried in vacuum oven.

Polyethylene and complex characterization

¹H-NMR spectrum was recorded on a Bruker BRX-100 AVANCE spectrometer. Elemental analysis for CHN was carried out by CHNO type Thermo Firingan 11112 EA microanalyzer. Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10 °C/min was used for the polyethylene 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 [28]. Calculation of $\Delta H_f / \Delta H_f^* \times 100$ gives the values of crystallinity where ΔH_f is the heat of fusion and $\Delta H_f^* = 69$ cal/g is the heat of fusion of 100% crystalline polyethylene. Intrinsic viscosity $[\eta]$ was measured in decaline at 135 °C using an Ubbelohde viscometer. M_v values were calculated through equation $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$ [29]. All the catalyst preparation and polymerization procedure were carried out under dried N₂.

Synthesis of bis(*N,N'*-2-fluorophenylimino)acenaphthene

To a solution of acenaphthoquinone (6.1 mmol) in methanol (20 mL), 2-fluoroaniline (12.2 mmol) and a trace amount of *p*-TsOH were added. The resulting solution was stirred at 45 °C for 48 h. A bright red precipitate appeared. The precipitated was filtered, washed with *n*-hexane and dried. The obtained reddish precipitate was



Scheme 1 Synthetic route to synthesize [bis(*N,N'*-2-fluorophenylimino)acenaphthene] nickel(II) dibromide

recrystallized from ethanol and the pure product was produced. The yield of the reaction was about 86%; $^1\text{H-NMR}$ (CDCl_3): δ 6.80 (dd, 2H), 7.17–7.45 (m, 8H), 7.84 (d, 2H), 7.91 (d, 2H). Anal. Calc. for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{F}_2$: C, 78.25; H, 3.83; N, 7.60 Found: C, 78.34; H, 3.85; N, 7.62.

Synthesis of [bis(*N,N'*-2-fluorophenylimino)acenaphthene] nickel(II) dibromide

Dimethoxyethanenickel dibromide (DME) NiBr_2 (1.2 mmol) and the ligand (1.2 mmol) were combined in a Schlenk flask under a nitrogen atmosphere to prepare Ni-based FI catalyst **A** (Scheme 1). CH_2Cl_2 (25 mL) was added to the solid mixture. The produced suspension was stirred for 24 h at room temperature. Solvent removal of the suspension resulted in the formation of a brown solid. The solid was washed with Et_2O several times and dried in vacuum. The yield of the reaction was about 70%; mp: >300 °C. NMR characterization was not possible because the compound is paramagnetic. Anal. Calcd. For $\text{C}_{24}\text{H}_{14}\text{Br}_2\text{N}_2\text{F}_2\text{Ni}$: C, 49.12; H, 2.40; N, 4.77. Found: C, 49.18; H, 2.44; N, 4.80. EIMS: MS (m/z): 579 (M), 506 (M^+-Br), 426 (M^+-2Br), 368 (M^+-NiBr_2).

Results and discussion

Effect of polymerizations parameters on activity

The experiments of ethylene polymerization with the prepared catalyst were carried out by dissolving the corresponding catalyst in toluene, followed by the injection of a toluene solution of different amount of TIBA, MAO and monomer gas to the Buchi reactor. After 30 min, reactions were terminated by shutting off the feed stream, followed by nitrogen purge and polymer precipitation using acidified (HCl) ethanol. Some results of polymerization are listed in Table 1.

The catalyst could not be used as a single component catalyst to polymerize ethylene, while Grubbs' catalysts with bulky phenyl group or larger groups at the *ortho* position of the phenoxy group can catalyze ethylene polymerization without cocatalyst [30]. It is clear that the prepared catalyst is different from mononuclear Grubbs' catalysts.

Table 1 Some specification of the obtained polymers

Pressure (bar)	Temperature (°C)	Activity (g PE/ mmol Ni h)	Crystallinity (%)	T_m (°C)	M_v
2	0	7.9×10^2	58	110	2.48×10^5
2	20	3.9×10^3	34	88	2.32×10^5
2	40	4.1×10^3	14	78	8.20×10^4
4	30	8.8×10^3	–	–	1.20×10^5
6	30	1.4×10^4	40	118	1.47×10^5
2	50	6.4×10^2	10	74	9.80×10^3

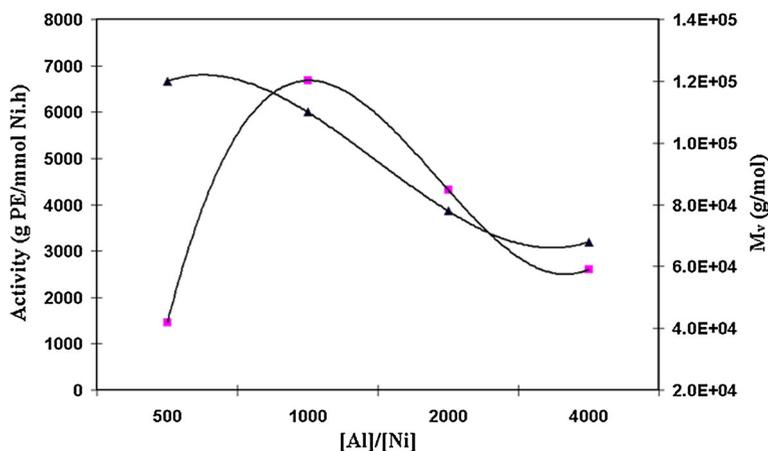


Fig. 1 Plots of polymerization activity (filled square) and M_v (filled triangle) of polyethylene versus $[Al]/[Ni]$ ratio. Polymerization temperature = 30 °C, polymerization time = 30 min, monomer pressure = 2 bar, $[Ni] = 7 \times 10^{-4}$ mmol, toluene = 250 mL

We have investigated the catalyst precursor by changing the ratios of MAO. Variation of the molar ratio of MAO/catalyst showed considerable effects on the catalyst activities and molecular weights of the resulted polymer. When the mole ratio of $[Al]/[Ni]$ is 500/1 at 30 °C, the catalytic activity is 1.5×10^3 g PE mmol^{-1} Ni h^{-1} and increase of the activity up to 6.6×10^3 g PE mol^{-1} Ni h^{-1} was observed by increase of the ratio of $[Al]/[Ni]$ to 1000/1, then decrease of the activity with the increase of ratio of $[Al]/[Ni]$ as shown in Fig. 1 is observed. At low concentration of MAO, the catalyst shows low activity, because there is no sufficient MAO to create all of active centers following to separate all of the active centers. But when the concentration of MAO increases by a certain value, on one hand, the plentiful MAO around the active center may block the monomer insertion, on the other hand, the free TMA in MAO can reduce the active center. So they can induce the decrease of catalytic activity.

Moreover, Chen and Marks [31] 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.

Figure 1 shows how the amount of MAO can dominate the catalyst activity. In addition, the viscosity average molecule weight (M_v) of the polymers decreased from 1.2×10^5 to 0.68×10^5 with increase of the [Al]/[Ni] ratio from 500/1 to 4000/1 (Fig. 1).

Similar to most transition metal-based catalysts, the Ni catalysts also suffered from the decay of catalytic activity at elevated polymerization temperatures [32, 33]. In this study, with the polymerization at the optimum value of [Al]/[Ni], the catalyst gave the polymer in a low yield at 0 °C. The optimum activity (6.7×10^3 g PE/mmol Ni h) was gained at 30 °C, and further increasing the temperature resulted in an intense decrease in catalytic activity (Fig. 2). Interestingly, at low polymerization temperatures no conspicuous changes in M_v of polymers were observed, suggesting the electronic effect of *ortho* fluorine substitutions phenyl ring on the N [34, 35].

As it is known, the β -hydride elimination rate directly affects the molecular weight of polymers. The introduction of F groups at the *ortho* position of phenyl groups can effectively suppress the β -hydride elimination by interaction with β -H of the growing polymer chain (Scheme 2). It gives rise to inhibiting the formation of olefin hydride complex intermediate which is susceptible to carry out various chain transfer reactions. Therefore, the transfer reactions can rarely occur and the molecular weight of the polymer is retained constant. Inversely, at higher temperatures due to the activation energy provided for β -H elimination to occur, the olefin hydride complex intermediate is simply formed and K_{CT} (chain transfer) is favored over K_{ins} (insertion) which led to the strong decrease of molecular weight. Additionally, the rotation of aryl rings is increased at higher polymerization temperature which might favor the olefin hydride complex intermediate formation (Scheme 3). As a result, the M_v of the polymer is decreased as the temperature increased which is due to the facilitated chain transfer reactions at the elevated temperature (Fig. 2). Accordingly, we get the highest (2.48×10^5) and lowest

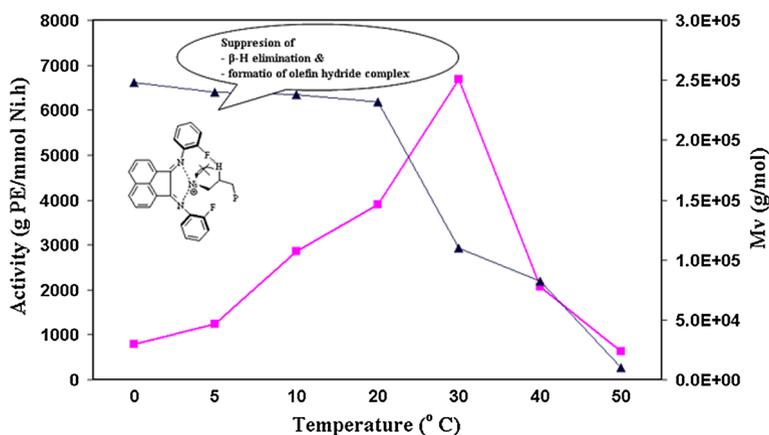
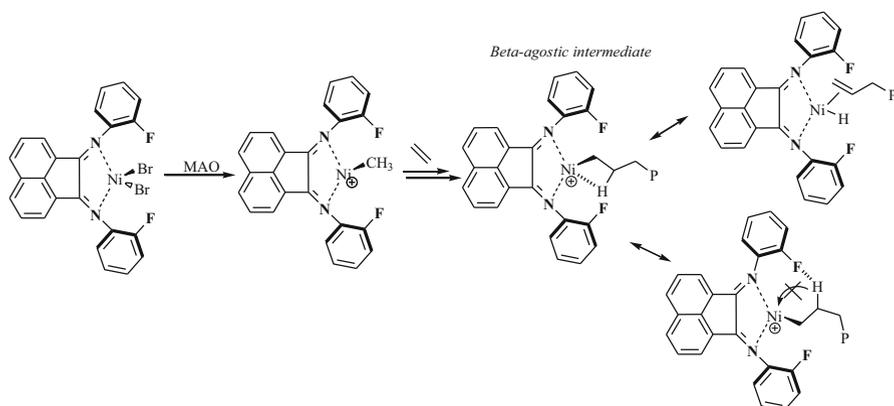
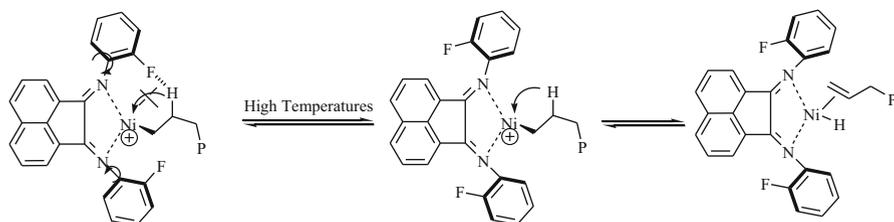


Fig. 2 Plots of polymerization activity (filled square) and M_v (filled triangle) of polyethylene versus reaction temperature. Polymerization time = 15 min, [Al]/[Ni] = 1000:1, monomer pressure = 2 bar, [Ni] = 7×10^{-4} mmol, toluene = 250 mL



Scheme 2 The electronically interaction between H- β and *ortho*-F-atom-substituted phenyl ring on the N

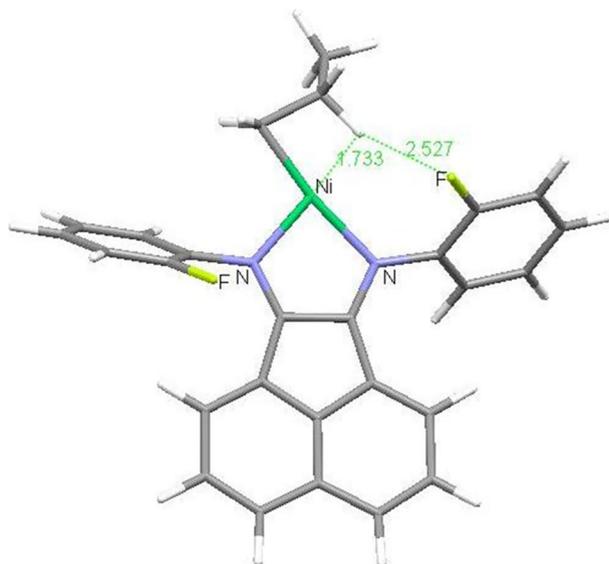


Scheme 3 Aryl ring rotation and more probability of olefin hydride intermediate formation

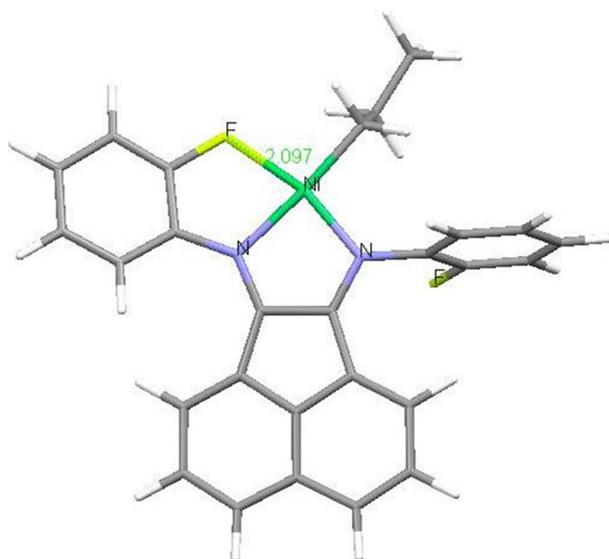
molecular weight (5.5×10^4) of polyethylene at 25 and 50 °C, respectively, while at the temperatures above 50 °C, polymer molecular weight was dropped dramatically and the catalyst activity was negligible.

Theoretical study by DFT

To support our proposed explanations and also investigate the effect of temperature on the catalyst structure, theoretical study was applied. To estimate the relative stabilities of β -agostic species, density functional theory (DFT) studies have been performed with GAUSSIAN 03 [36] program using B3LYP method of theory with the LanL2dz basis set at room temperatures and 75 °C, respectively (Schemes 4, 5). DFT studies showed that the interaction between β -H of the growing polymer chain and *ortho*-fluorine of the ligand is predictable to produce higher molecular weight polyethylene by the effective suppression of β -H transfer to the metal or incoming monomer (*ortho*-F/ β -H distance 2.52 Å) (Van der Waals radii of H and F are 1.20 and 1.47 Å, respectively) Schemes 2 and 4 show this interaction. A similar result has been found in titanium complexes with β -diketiminato ligands [37] and phenoxyimine ligands [35] and also our previous work with zirconium phenoxyimine ligands [38].



Scheme 4 DFT-optimized structure of a cationic species structure at 25 °C, $E = -41,334.780$ eV



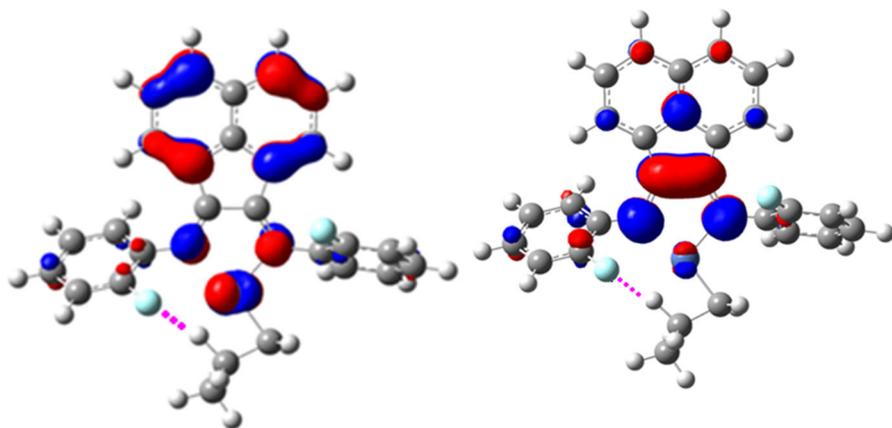
Scheme 5 DFT-optimized structure of a cationic species structure. $T \geq 50$ °C, $E = -41,334.591$ eV

Although previous studies demonstrated that main reason for obtaining low molecular weight polymer is attributed to higher β -H transfer reactions, in the present study we proposed, that at higher temperature (above 50 °C), production of low molecular weight polyethylene is not due to the high β -H transfer reactions, but

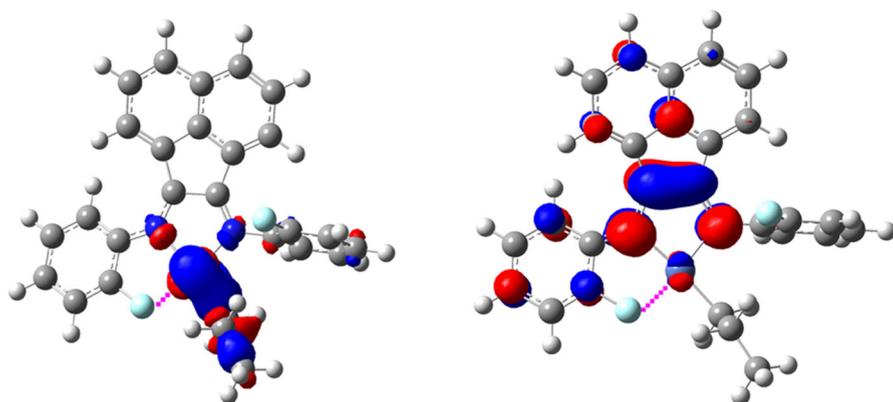
it is due to the coordination of fluorine atom with nickel giving rise to hindrance upon axial coordination sites. As illustrated in Scheme 5, at higher temperature one of the *ortho*-fluorinated aniline rings by possessing planar position, aids fluorine atom to situate at close proximity to the nickel (*ortho*-F/Ni distance 2.09 Å). Additionally, coordination of *ortho*-F to Ni can be also proved by lower positive QEq charge on Ni at higher temperature, at higher temperature the QEq charge on the central metal is +0.39 which declined to QEq charge 0.28 at room temperature. As a result, hindrance of axial position caused by *ortho*-F substitution of the ligand over central metal prevents proper monomer insertion to the active centers following to diminish the catalyst activity as well as molecular weight of the resulting polymer. In the other words, catalyst deactivation is responsible to produce low molecular weight PE at high temperatures. One more fact is that since the calculated charge on hydrogen and fluorine atoms at room temperature is +0.176 and -0.260, respectively, fluorine is better ligand than hydrogen, leading to make stronger coordination bonding with nickel. So, F coordination does not has enough tendency to separate from nickel even while the coming monomer is next to the active center. To the best of our knowledge, this is the first report of catalyst deactivation mechanism for fluorinated α -dimine Ni catalysts at high temperatures.

Another evidence for unfeasibility of β -H transfer reactions to the metal center at high temperature is perceived from longer distance between β -H of the growing polymer chain and nickel (β -H/Ni 2.29 Å at high temperature versus 1.73 Å at room temperature). Schemes 6 and 7 represent the optimized β -agostic structure of the cationic species at low and high temperatures.

According to the literature, it has already been reported that β -H transfer is the dominant chain transfer mechanism for ethylene polymerization with non-fluorinated Zr and Ti-FI catalysts, whereas a chain transfer to aluminum can be predominant in the case of the non-fluorinated FI catalyst. However, fluorinated LTM catalyst behavior in terms of influential role of F substitution has never been reported so far. In addition, all the literatures have been investigating the promoting



Scheme 6 HOMO (left figure) and LUMO (right figure) molecular orbitals of the optimized β -agostic structure at room temperature (*ortho*-F/H- β interaction possibility). $E_{\text{HO}} = -9.25$ eV, $E_{\text{LU}} = -6.32$ eV



Scheme 7 HOMO (left figure) and LUMO (right figure) molecular orbitals of the optimized β -agostic structure above 50 °C (*ortho*-F/Ni interaction possibility). $E_{\text{HO}} = -9.02$ eV, $E_{\text{LU}} = -6.48$ eV

halogen substitution effects on polymer molecular weight and catalyst activity at low temperature, while herein with precise practical and computational study, not only the promoting effects, but also the possibility of destructive role of F substitution on catalyst behavior at higher polymerization temperature which is critical for commercial application of such catalysts is elaborated.

To understand the kinetic behavior of ethylene polymerization, polymerization was carried out at the different reaction times while the other conditions were kept constant. The catalyst activity rises quickly to its maximum at the beginning of the polymerization (5 min). Afterward, its activity drops slightly and keeps almost stable for 10–30 min. Then, the activity drops sharply and after 1 h it was relatively negligible (Fig. 3). Owing to presence of substituted fluorines on the ligand backbone, the electropositivity of the metal center might be increased. On the other hand, lack of bulky alkyl substitutions on the ligand backbone leads to provide enough free space for propagation. Therefore, the quickly progress of activity might be attributable to the higher electropositivity and a more open spatial structure of the metal center which facilitates the monomer coordination. Moreover, M_v was linearly increased with time suggesting the living polymerization behavior. In general, fluorinated catalysts have been discovered to promote unprecedented living ethylene and propylene polymerizations, resulting in the formation of functionalized polymers and block copolymers from ethylene [35, 39].

Unexpectedly, high ethylene pressure did not significantly affect the activity of the fluorinated Ni catalyst while at low ethylene pressure the influence on the activity as well as molecular weight was remarkable (Fig. 4). Although the effect of monomer concentration on activity remains clear, it was difficult to make an interpretation of such a behavior at high monomer pressure. In addition, as can be seen in Fig. 4, there is a stable zone for activity at the pressures above 5 bars. However, as expected this trend is ascending at lower ethylene pressure.

A dramatic effect on the crystallinity of the resulting polymer was observed with increasing of the polymerization temperature. The crystallinities and melting points

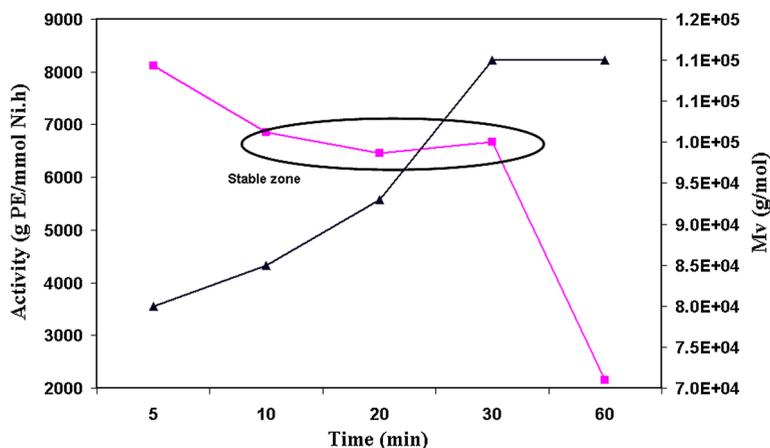


Fig. 3 Plots of relationship between polymerization activity (filled square) and M_n (filled triangle) of polyethylene with polymerization time. Temperature = 30 °C, [Al]/[Ni] = 1000:1, monomer pressure = 2 bar, [Ni] = 7×10^{-4} mmol, toluene = 250 mL

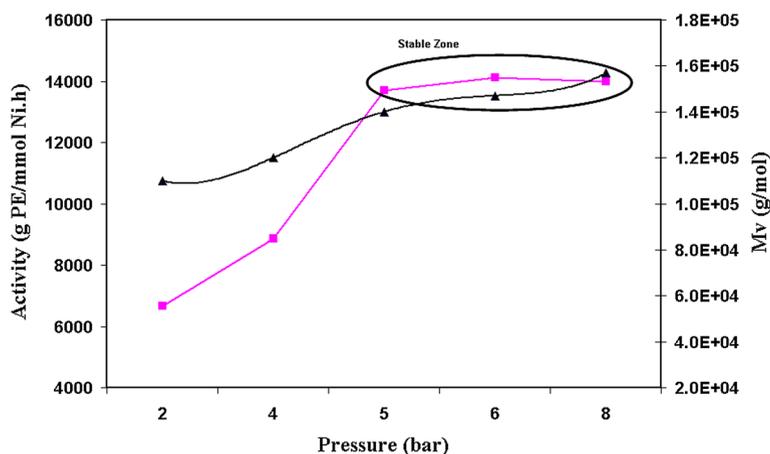


Fig. 4 Plots of relationship between polymerization activity (filled square) and M_n (filled triangle) of polyethylene with polymerization pressure. Temperature = 30 °C, [Al]/[Ni] = 1000:1, [Ni] = 7×10^{-4} mmol, time = 30 min

of the polymers obtained at the polymerization temperatures of 0, 20 and 40 °C were 53, 34, and 14% and 110, 88 and 78 °C, respectively (Table 1). It substantiated our hypothesis shown in Scheme 3 about the influence of fluorine atom and temperature on the polymerization as well as polymer properties. As shown in Scheme 3, higher temperatures facilitate chain transfer reactions through the formation of olefin hydride complex intermediate. Therefore, chain walking would occur which leads to the production of highly branched polyethylene with low crystallinity. Inversely, at low polymerization temperature due to the electronic interaction between F and β -H of growing polymer chain, seldom olefin hydride

complex formation is in favor of monomer insertion giving rise to produce PE with high crystallinity and melting point.

Conclusion

The prepared fluorinated acenaphthoquinone-based α -diimine Ni-catalyst displayed moderate ethylene polymerization activities. Although the interaction between *ortho*-F and the β -H on a growing polymer chain suppresses the β -H elimination, but the transition state of interaction is probably disfavored for coordination of ethylene to the active centers which moderate the polymerization activity. DFT studies revealed that the probable coordination of fluorine atom to the central metal at high temperatures gives rise to a hindrance upon axial coordination sites which leads to make an obstacle for monomer insertion resulting is lower both catalyst activity and molecular weight of the polymer. The electronic interaction of β -H and F could control branching degree of the resulted polymer by prohibiting the formation of olefin hydride complex intermediate at lower polymerization temperatures. The crystallinity and melting point of the polymer were depended on polymerization temperature profoundly.

Acknowledgements The authors wish to thank Ferdowsi University of Mashhad for financial support and staff of DSC Lab of Engineering Department of Chemical Engineering Faculty of Ferdowsi University of Mashhad for their kind help.

References

1. Kaminsky W (2008) Trends in polyolefin chemistry. *Macromol Chem Phys* 209:459–466
2. Tuchbreiter A, Mülhaupt R (2001) The polyolefin challenges: catalyst and process design, tailor-made materials, high-throughput development and data mining. *Macromol Symp* 173:1–20
3. Ahmadjo S (2016) Preparation of ultra high molecular weight amorphous poly(1-hexene) by a Ziegler–Natta catalyst. *Polym Adv Technol* 27:1523–1529
4. Coates GW (2000) Control of polyolefin stereochemistry using single-site metal catalysts. *Chem Rev* 100:1223–1252
5. Hoff R, Mathers RT (2010) Handbook of transition metal polymerization catalyst. Wiley-VCH, Weinheim
6. Britovsek GJP, Gibson VC, Wass DF (1999) The search for new-generation olefin polymerization catalysts: life beyond metallocenes. *Angew Chem Int Ed* 38:428–477
7. Busico V (2007) Catalytic olefin polymerization is a mature field. Isn't it. *Macromol Chem Phys* 208:26–29
8. Johnson LK, Killian CM, Arthur SD, Feldman J, McCord EF, McLain SJ, Kreutzer K A, Bennett AMA, Coughlin EB, Ittel SD, Parathasarathy A, Tempel DJ, Brookhart M (1996) Pat Appl. WO1996023010, DuPont
9. Johnson LK, Killian CM, Brookhart M (1995) New Pd (II)- and Ni (II)-based catalysts for polymerization of ethylene and alpha-olefins. *J Am Chem Soc* 117:6414–6415
10. Mecking S (2001) Olefin polymerization by late transition metal complexes. *Angew Chem Int Ed* 40:534–540
11. Peuckert M, Keim W (1983) A new nickel complex for the oligomerization of ethylene. *Organomet* 2:594–597
12. Deng L, Woo TK, Cavallo L, Margl PM, Ziegler T (1997) The role of bulky substituents in Brookhart-type Ni(II) diimine catalyzed olefin polymerization: a combined density functional theory and molecular mechanics study. *J Am Chem Soc* 119:6177–6186

13. Ittel SD, Johnson LK, Brookhart M (2000) Late-metal catalysts for ethylene homo- and copolymerization. *Chem Rev* 100:1169–1204
14. Rieger BL, Saunders BL, Kacker S, Striegler S (eds) (2003) Late transition metal polymerization catalysis. Wiley-VCH, Weinheim
15. Takeuchi D (2010) Recent progress in olefin polymerization catalyzed by transition metal complexes: new catalysts and new reactions. *Dalton Trans* 39:311–328
16. Barabanov AA, Semikolenova NV, Bukatov GD, Matsko MA, Zakharov VA (2012) Ethylene polymerization over homogeneous bis(imino)pyridine vanadium catalysts: data on the number and reactivity of active sites. *J Polym Res* 19:9998–10007
17. Johnson LK, Mecking S, Brookhart M (1996) Copolymerization of ethylene and propylene with functionalized vinyl monomers by palladium (II) catalysts. *J Am Chem Soc* 118:267–268
18. Camacho DH, Salo EV, Ziller JW, Guan Z (2004) Cyclophane-based highly active late-transition-metal catalysts for ethylene polymerization. *Angew Chem Int Ed* 43:1821–1825
19. Wang C, Friedrich S, Younkin TR, Li RT, Grubbs RH, Bansleben DA, Day MW (1998) Neutral nickel(II)-based catalysts for ethylene polymerization. *Organomet* 17:3149–3151
20. Gibson VC, Spitzmesser SK (2003) Advances in non-metallocene olefin polymerization catalysis. *Chem Rev* 103:283
21. George JP, Britovsek SPD, Baugh OH, Vernon CG, Duncan FW, Andrew JPW, Williams D (2003) The role of bulky substituents in the polymerization of ethylene using late transition metal catalysts: a comparative study of nickel and iron catalyst systems. *Inorg Chim Acta* 345:279–291
22. Mecking S, Johnson LK, Wang L, Brookhart (1998) Mechanistic studies of the palladium-catalyzed copolymerization of ethylene and α -olefins with methyl acrylate. *J Am Chem Soc* 120:888–889
23. Popeney C, Guan Z (2005) Ligand electronic effects on late transition metal polymerization catalysts. *Organomet* 24:1145–1155
24. Helledorfer H, Backhaus J, Alt HG (2003) (α -Diimine) nickel(II) complexes containing chloro substituted ligands as catalyst precursors for the oligomerization and polymerization of ethylene. *Inorg Chim Acta* 351:34–42
25. Khoshsefat M, Zohuri GH, Ramezani N, Ahmadjo S, Haghpana M (2016) Polymerization of ethylene using a series of binuclear and a mono nuclear Ni(II)-based catalysts. *J Polym Sci Polym Chem* 54:3000–3011
26. Zohuri GH, Damavandi S, Dianat E, Sandaroos R, Ahmadjo S (2011) Late transition metal catalyst based on cobalt for polymerization of ethylene. *Inter J Polym Mat* 60:776–786
27. Sandaroos T, Cuenca T, Zohuri GH, Damavandi S, Ahmadjo S (2012) Titanium (IV) and nickel (II) catalysts based on anilinetropone ligands. Chapter 10, Polymerization, De Souza Gomes A, InTech publication
28. Justino T, Dias AR, Ascenso J, Marcues MM, Tait PJT (1997) Polymerization of ethylene using metallocene and aluminoxane systems. *Polym Int* 44:407–412
29. Brandrup J, Immergut EH (1998) Polymer handbook, VII, 3rd edn. Wiley, New York, pp 1–7
30. Damavandi S, Zohuri GH, Sandaroos R, Ahmadjo S (2012) Novel functionalized bis(imino)pyridine cobalt(II) catalysts for ethylene polymerization. *J Polym Res* 19:9796–9800
31. Chen EYX, Marks TJ (2000) Cocatalysts for metal-catalyzed olefin polymerisation: activators, activation processes, and structure-activity relationships. *Chem Rev* 100:1391–1434
32. Chen AP, Gua L, Jie Y (2012) Polymerization of 1, 3-butadiene catalyzed by cobalt (II) and nickel (II) complexes bearing imino-or amino-pyridyl alcohol ligands in combination with ethylaluminum sesquichloride. *Organomet Chem* 705:51–58
33. Liu H, Jia X, Wang F, Dai Q, Wang B, Bi J, Zhang C, Zhao L, Bai C, Hu Y, Zhang X (2013) Synthesis of bis(*N*-arylcaboximidoylchloride)pyridine cobalt(II) complexes and their catalytic behavior for 1,3-butadiene polymerization. *Dalton Trans* 42:13723–13732
34. Ishii SI, Furiyama R, Matsukawa N, Saito J, Mitani M, Tanaka H, Fujita T (2003) Ethylene and ethylene/propylene polymerization behavior of bis(phenoxy-imine) Zr and Hf complexes with perfluorophenyl substituents. *Macromol Rapid Commun* 24:452–456
35. Saito J, Mitani M, Mohri J, Ishii S, Yoshida Y, Matsugi T, Kojoh S, Kashiwa N, Fujita T (2001) Highly syndiospecific living polymerization of propylene using a titanium complex having two phenoxy-imine chelate ligands. *Chem Lett* 30:576–582
36. Frisken MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Scalmani T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone B, Mennucci B, Cossi M, Rega GA, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Hada M, Ehara M, Toyota K,

- Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03. Gaussian Inc, Wallingford
37. Kissin YV, Qian C, Xie G, Chen X (2006) Multi-center nature of ethylene polymerization catalysts based on 2,6-bis(imino)pyridyl complexes of iron and cobalt. *J Pol Sci Part A Polym Chem* 44:6159–6170
38. Zohuri GH, Damavandi S, Sandaroos R, Ahmadjo S (2011) Ethylene polymerization using fluorinated FI Zr-based catalyst. *Polym Bull* 66:1051
39. Zohuri GH, Damavandi S, Sandaroos R, Ahmadjo S (2014) Synthesis of high molecular weight polyethylene using FI catalyst. *Polyolefin J* 1:25–32