J Polym Res (2012) 19:9796
DOI 10.1007/s10965-011-9796-y

ORIGINAL PAPER

Novel functionalized bis(imino)pyridine cobalt(II) catalysts for ethylene polymerization

Saman Damavandi · Gholam Hossein Zohuri · Reza Sandaroos · Saied Ahmadjo

Received: 20 April 2011 / Accepted: 16 November 2011 / Published online: 22 February 2012

Abstract This report describes synthesis and ethylene polymerization in the various conditions by two novel 2,6-bis(imino)pyridine (BIMP) catalysts B and C based on cobalt activated by methylaluminoxane (MAO) in a slurry semi-batch reactor. The catalyst activities as well as polymer properties were affected dramatically by electronic effects of the attached substitutions on the *para*-position of the pyridine ring. Theoretical study exhibited more positive charge on the central metal of the catalyst B resulted in higher activity at the expense of lower thermal stability and lifetime. The polymer obtained using the catalysts exhibited high molecular weight and almost narrow molecular weight distribution (MWD) ranging from 2.35 to 4.10 at the employed polymerization conditions. The highest and lowest molecular weight of the obtained polymers were produced by the catalyst A and C respectively. Hydrogen could slightly increase the catalyst activities with the exception of the catalyst B. The catalyst C bearing electron-donor OMe substitution at the *para*-position of the pyridine ring, produced PE with narrower PDI relative to the polymer resulted by catalysts A and B.

Keywords Polyethylene · BIMP–Co catalyst · Late transition metal catalyst

Introduction

Early transition-metal Ziegler–Natta systems and chromium based catalysts, both exploited commercially over many years, have been joined recently by several families of highly active late-transition metal catalysts based, for example, on iron, cobalt and nickel [1–3]. Amongst these new systems, the bis(imino)pyridine iron and cobalt systems, discovered independently by Brookhart, Bennett and Gibson [4–7].

In 1995 Brookhart and coworkers reported new Ni(II)- and Pd(II)-based catalysts bearing bulky diimine ligands for ethylene polymerization [8, 9]. These catalysts are highly active and produce high molecular weight polymers. The bulky substituents on the aryl groups of the ligands block an associative olefin exchange, thus effectively retarding chain transfer pro-cesses. Furthermore, the microstructure of the polymers produced is a function of temperature, monomer pressure, steric bulkiness of the auxiliary ligands, and transition metal center. Variation of these factors allows access to a range of linear and branched polyethylene. Although many researches have been devoted to the modification of BIMP catalysts, mostly attention has been paid to the groups attached to the amine nitrogen donors [10–12]. For instance, Bennett and co-workers reported an imidazolyl substituted derivative that showed similar activity to its ketimine analogue [13]. Gibson and co-workers studied systematic variations at the imine carbon position [14]. Ionkin and co-workers investigated

S. Damavandi (✉)
Department of Chemistry, Faculty of Sciences, University of Isfahan,
Isfahan 81746-73441, Iran
e-mail: Saman_Damavandi@yahoo.com

G. H. Zohuri
Department of Chemistry, Ferdowsi University of Mashhad,
Mashhad, Iran

G. H. Zohuri
e-mail: ghzohuri@ippi.ac.ir

R. Sandaroos
Department of Chemistry, Faculty of Science, Birjand University,
Birjand, Iran

S. Ahmadjo
Department of Catalyst, Iran Polymer and Petrochemical Institute,
Tehran, Iran

ethylene polymerization using a series of nitro-substituted bis (imino)pyridine complexes based on iron [15].

However, less attention has been directed towards introducing functional groups to the pyridine ring of the ligand. In the present study, the synthesis, structure, and precise ethylene polymerization behavior of new BIMP catalysts based on cobalt containing electron-withdrawing and electron-donor substitutions attached to the pyridine ring were reported. Although the replacement of *para* substituents of the pyridine ring doesn't provide any significant change in steric bulk, the electronic effects caused remarkable variations in catalyst activity as well as polymer characteristics. Furthermore, with the aid of theoretical study, the charges on the central metal of the catalysts were calculated and discussed.

Experimental

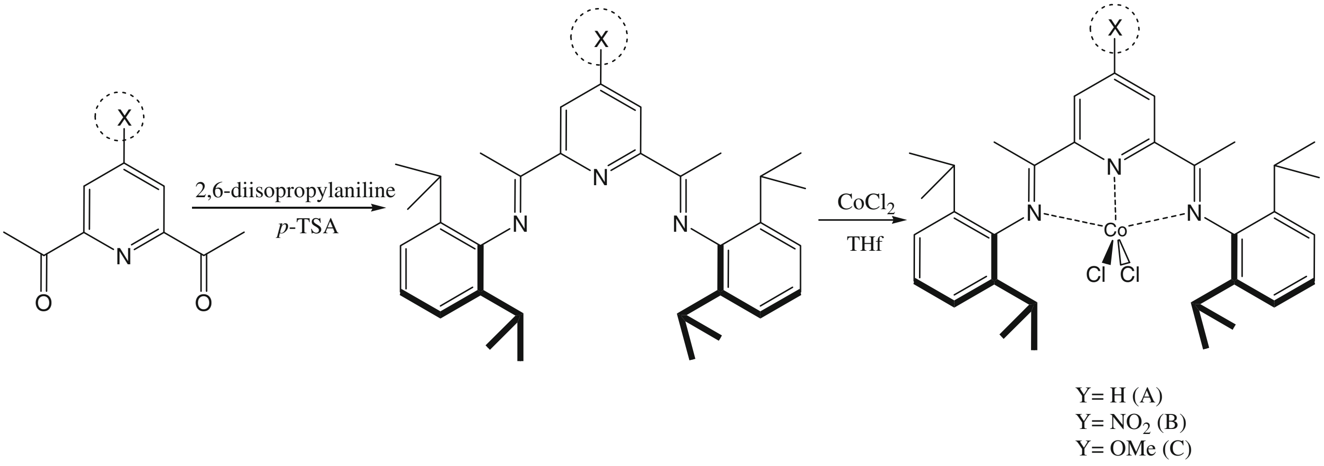
General methods

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. The viscosity average molecular weight (Mv) of some polymer samples were determined according to the previous report [16, 17]. Intrinsic viscosity [η] was measured in decaline at 135 °C using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10 °C/min instrument was used for polymer characterization. Mv values and degree of crystallinity of a polyethylene sample were calculated according to our previous report [17]. Elemental analysis for CHN was carried out by the CHNO type from the Helaus Co. ^{1}H NMR spectra were recorded on a Bruker spectrometer (500 MHz) at 293 K. 2,6-Lutidine, MAO (10%), 2,4,6-trimethylaniline and other chemicals were purchased from Sigma-Aldrich Chemical Co. The general procedure of polymerization was to dissolve of precatalyst in toluene (300 mL) and adding of MAO (10 wt% in toluene) to produce an orange solution. The reactor was purged with ethylene, and the contents were stirred and maintained under ethylene for the duration of the polymerization. The polymerization was terminated by the addition of aqueous hydrogen chloride. The solid PE was collected by filtration, washed with methanol (50 mL), and dried.

Ligand and catalyst preparation

4-Nitro-2,6-diacethylpyridine and 4-Methoxy-2,6-diacethylpyridine were synthesized according to our recent report [18].

2,6-Diacethyl pyridine bis(2,6-diisopropylphenylimine) (a): To a solution of 2,6-diacethylpyridine (0.98 g, 6.1 mmol) in methanol (30 ml), 2,6-diisopropylaniline (12.4 mmol, 2.38 ml) and a trace amount of 4-toluenesulfonic acid were added. The resulting yellow solution was stirred at room temperature for 2 days, a white precipitate had formed. The precipitated was filtered, washed with cold methanol, and dried. A pale yellow solid was obtained. ^{1}H NMR study revealed that both the monoamine and diimine products were present. Therefore, the resulting solid was dissolved in boiling mixture of methanol and chloroform. Addition of chloroform was continued until the solid was dissolved following to excess addition of 2,6-diisoropylaniline (6.1 mmol, 1.19 ml). The solution was refluxed for 5 days. The solvent was removed, a yellow solid was obtained that washed with n-hexane and dried (70% yield). ^{1}H NMR ($CDCl_3$): δ 1.2 (d, 24H), 2.3 (s, 6H), 2.8 (m, 4H), 7–7.2 (m, 6H), 7.88 (t, 1H), 8.4 (d, 2H). Anal. ($C_{33}H_{43}N_3$) calcd: C, 82.32; H, 8.94; N, 8.73. Found: C=82.33%, H=9.11%, N=8.68%.



Scheme 1 Synthetic route to substituted BIMP-Co catalysts

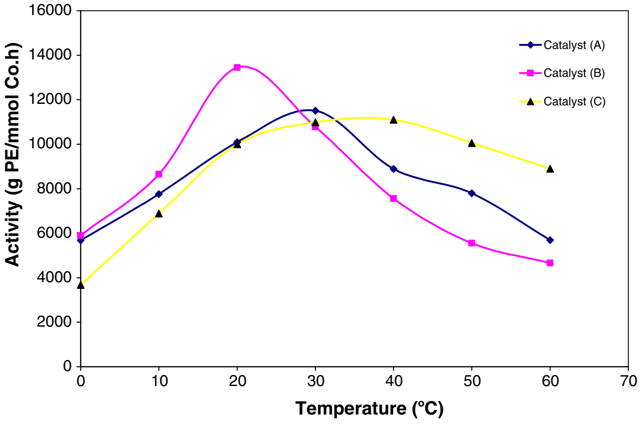


Fig. 1 Effect of temperature on the average rate of polymerization. Polymerization conditions: Polymerization time = 30 min, monomer pressure = 5 bar, [Al]:[Co]=3000:1, [Co]=0.35×10^{-3} mmol, toluene = 300 mL

4-Nitro-2,6-diacethyl pyridine bis(2,6-diisopropylphenylimine) (b): By using the same procedure described above, the compound b was obtained in 76% yield as an orange solid. ^{1}H NMR ($CDCl_3$): d, 8.70 (s, 2H), 7.25–6.85 (m, 6H), 3.02 (m, 4H), 2.25 (s, 6H), 1.2 (d, 24H). Anal. ($C_{33}H_{42}N_4O_2$) calcd: C, 75.25; H, 8.04; N, 10.64. Found: C, 74.86; H, 8.11; N, 10.44.

4-Methoxy-2,6-diacethyl pyridine bis(2,6-diisopropylphenylimine) (c): By using the same procedure described above, the compound c was obtained in 74% yield as a pale brown solid. ^{1}H NMR ($CDCl_3$): d, 7.42 (s, 2H), 7.20–6.80 (m, 6H), 3.65 (s, 3H), 3.10 (m, 4H), 2.25 (s, 6H), 1.25 (d, 24H). Anal. ($C_{33}H_{45}N_3O$) calcd: C, 79.80; H, 8.86; N, 8.21. Found: C, 79.27; H, 8.93; N, 8.27.

Catalyst synthesis

[2,6-diacethylpyridinebis(2,6-diisopropylphenylimine)] cobalt(II) dichloride (A)

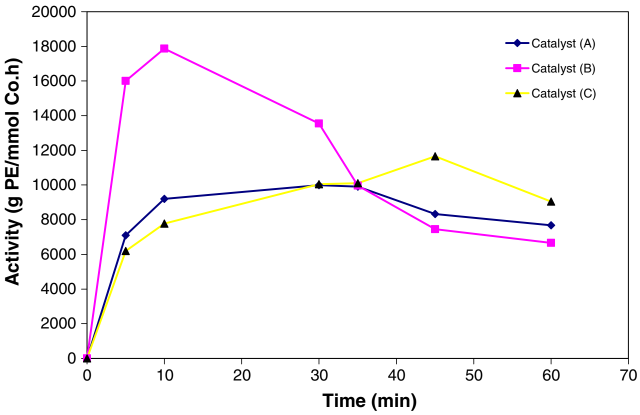


Fig. 2 Rp versus time. Polymerization conditions: monomer pressure = 5 bar, [Al]:[Co]=3000:1, [Co]=0.35×10^{-3} mmol, toluene = 300 mL

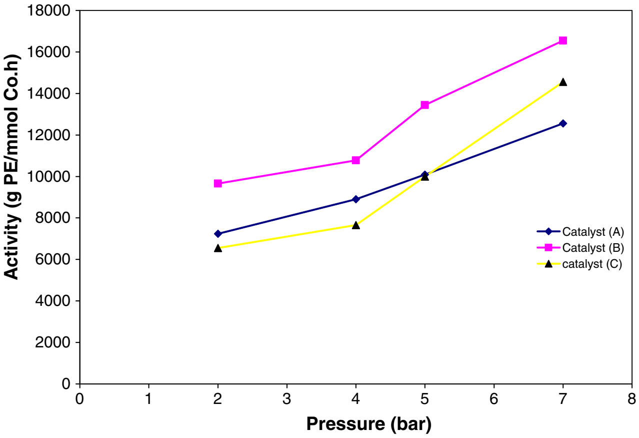


Fig. 3 Effect of monomer pressure on the polymerization behavior. Polymerization conditions: temperature = 30 °C, polymerization time = 30 min, [Al]:[Co]=3000:1, [Co]=0.35×10^{-3} mmol, toluene = 300 mL

In a dry, oxygen free atmosphere, $CoCl_2$ (anhydrous, 1.078 mmol) was dissolved in dry THF. [2,6-Diacethylpyridinebis(2,6-diisopropylphenylimine)], the ligand, (1.156 mmol) was added. The mixture was stirred for 3 days at room temperature and a dark blue precipitate was formed. The solid product was filtered, washed with dry *n*-hexane and dried under N_2. The solid catalyst of [2,6-diacethylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride (yield 75%) was obtained. ^{1}H NMR (CD_2Cl_2, broad singlets are observed in each case): δ 114.91 (2H, Py-*H*m), 49.85 (1H, Py-*H*p), 10.01 (4H, Ar-*H*m), 4.41 (6H, \NCC*H*3), -8.88 (2H, Ar-*H*p), -16.74 (12H, *i*Pr-*Me*), -18.22 (12H, *i*Pr-*Me*), -81.92 (4H, *i*Pr-C*H*). Anal. ($C_{33}H_{43}Cl_2CoN_3$) calcd: C, 64.81; H, 7.09; N, 6.87%. Found: C=64.66%, H=6.78%, N=6.90%.

[4-Nitro-2,6-diacethylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride (B): By using the same

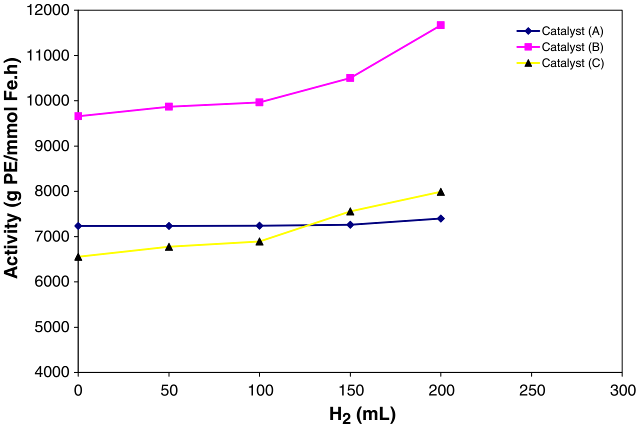


Fig. 4 Effect of hydrogen on the average activity. Polymerization conditions: Polymerization time = 30 min, monomer pressure = 2 bar, [Al]:[Co]=3000:1, [Co]=0.35×10^{-3} mmol, toluene = 300 mL

Table 1 Correlation between catalyst activities and catalyst charges

Catalyst	Activity (g PE/mmol Co. h)	QEq charge on Co
A	34,270	0.3212
B	56,250	0.3467
C	28,500	0.3058

Polymerization conditions: monomer pressure = 5 bar, polymerization time = 30 min, [Al]:[Co]=3000:1, [Co]=0.35×10^{-3} mmol, toluene = 300 mL.

procedure described for the synthesis of catalyst A, complex B was obtained in 74% yield as an orange solid.

^{1}H NMR (CD_2Cl_2, broad singlets are observed in each case): δ 96.55 (2H, Py-*H*m), 10.15 (4H, Ar-*H*m), 4.75 (6H, NdCC*H*3), -7.22 (2H, Ar-*H*p), -14.62 (12H, *i*Pr-*Me*), -16.15 (12H, *i*Pr-*Me*), -80.44 (4H, *i*Pr-C*H*). Anal. ($C_{33}H_{42}Cl_2CoN_4O_2$) calcd: C, 60.37; H, 6.45; N, 8.53%. Found: C=60.24, H=6.54, N=8.48%.

[4-Methoxy-2,6-diacethylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride (C)

By using the same procedure described for the catalyst A, complex C was obtained in 70% yield as a brown solid. ^{1}H NMR (CD_2Cl_2, broad singlets are observed in each case): δ 112.25 (2H, Py-*H*m), 11.02 (4H, Ar-*H*m), 4.52 (6H, NCC*H*3), -6.75 (2H, Ar-*H*p), -17.31 (12H, *i*Pr-*Me*), -16.70 (12H, *i*Pr-*Me*), -22.5 (3H, OMe), -80.44 (4H, *i*Pr-C*H*). Anal. $C_{34}H_{45}Cl_2CoN_3O$) calcd: C, 63.65; H, 7.07; N, 6.55%. Found: *C*=63.69, *H*=7.13, *N*=6.49%.

Scheme 1. Synthetic procedure for the catalysts A-C

Results and discussion

Ethylene polymerization reactions using the prepared catalysts A-C were carried out at the different polymerization conditions. All three catalysts exhibited high activity for ethylene polymerization at low and high pressure runs. The catalysts gave the activities in the order of: catalyst B > catalyst A > catalyst C.

For all the catalysts, the effect of reaction temperature, reaction time, ethylene pressure and hydrogen concentration on catalyst activity were studied. The influence of polymerization temperature on activity was investigated at the reaction temperatures between 0 and 60 °C, while the [Al]/[Co] molar ratio was kept constant at [Al]/[Co]=3000:1. As it can be seen in Fig. 1, the highest productivity of the catalysts A, B and C were occurred at about 30, 20 and 45 °C respectively. In the case of catalyst A, the activity increased with polymerization temperature reaching a maximum at 30 °C, but at higher temperature, activity was reduced due to the increase in catalyst deactivation rate as known for most olefin polymerization catalysts. Activity of the catalyst B bearing *p*-NO_2 substitution reaches to a maximum value at 20 °C and further increase of temperature led to a dramatic decrease in its activity. It can be concluded that introducing the *p*-OMe substitution at the *para*-position of the pyridine ring could increase the thermal stability of the catalyst C. The catalyst C bearing *p*-OMe substitution exhibited more stable trend toward increase of polymerization temperature, the activity was almost stable at the temperatures between 20 and 50 °C. Higher activity of the catalyst B was offset by lower thermal stability and life time.

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 catalysts. According to the Fig. 2, as reaction time increases, the activity increases and after reaching a certain maximum time, it decreases. At the monomer pressure of 5 bar and ambient temperature, these maximums for the catalysts A–C are around 30, 10 and 45 min, respectively.

The influence of monomer pressure between 2 and 7 bars on the catalyst behavior was studied. The polymerization behavior is shown in Fig. 3. Catalyst activities increased with ethylene pressure with the similar trend which can be explained since catalyst active sites were exposed to higher ethylene concentration at higher pressure.

Table 2 Some characterization of the resulted polyethylene

Sample	Pressure (bar)	Temperature (°C)	Crystallinity%	M_v	T_m (°C)	PDI
(cat.A)	2	30	66	3.2×10^4	132	–
(cat.A)	5	30	63	4.1×10^4	130	3.21
(cat.A)	7	30	60	4.5×10^4	135	–
(cat.A)	7	50	58	4.3×10^4	130	–
(cat. B)	5	30	62	3.9×10^4	132	3.76
(cat. B)	5	50	56	3.7×10^4	125	–
(cat B)	7	30	55	3.8×10^4	131	4.10
(cat C)	5	30	60	3.5×10^4	125	–
(cat C)	7	30	57	3.7×10^4	130	2.35
(cat C)	7	50	55	3.1×10^4	127	2.84

Polymerization conditions: polymerization time = 60 min, [Al]:[Co]=3000:1, [Co]=0.35×10^{-3} mmol, toluene = 300 mL.

Ethylene polymerization was carried out using different amount of hydrogen as a chain transfer agent. As it can be seen in Fig. 4, higher amount of hydrogen could increase the activity of the catalysts B and C to some extent. A reasonable explanation for this enhancement effect might be the more homogeneous reaction conditns [19]. However, 2,1-reinsertion of short olefin branches, terminated by β-H elimination which can still coordinate to the active centers, is probable [20]. Activity of the catalyst A was not sensitive to the amount of hydrogen.

With the aid of Gaussian software [21] the most stable conformations and QEq charges of catalysts A–C were calculated. As expected, attachment of the nitro group led to a more electrophilic metal center (Table 1).

The presence of electron-withdrawing nitro substituent on the pyridine ring of the catalyst is considered to be highly beneficial for increasing the catalyst activity since the introduction of electron-withdrawing group on the ligand structure results in an increase in electrophilicity of the catalyst central metal. Not only the catalyst activities and catalyst behavior during the polymerization were remarkably affected by different substitution at the *para*-position of the pyridine ring, but the polymer characteristics such as molecular weight, degree of crystallinity and melting point were influenced (Table 2). M_v of the obtained polymer follows A > B > C. Catalyst A produced PE with the highest M_v. Furthermore, it can be concluded that the molecular weight and polydispersity of the polyethylene obtained from the synthesized catalysts were affected by the catalysts structure. The catalyst C bearing electron-donor OMe substitution at the *para*-position of the pyridine ring, produced PE with narrower PDI relative to polymer resulted using the other prepared catalysts.

Conclusion

Attaching the NO_2 and OMe substitution at the *para*-position of the pyridine ring caused the activity of the catalyst to vary. Polymerization reactions using the prepared catalysts were carried out at the different conditions of temperature, monomer pressure, polymerization time, and H_2 concentration. Although the catalyst B showed the highest activity, lower thermal stability and lifetime was observed for the catalyst. The activity of the catalyst C toward increasing the temperature was surprisingly stable. Hydrogen could increase the activity of the catalysts B and C to some extent, while the activity of the catalyst A was less sensitive to the hydrogen concentration. Theoretical investigations revealed a more positive charge on the central metal of the catalyst B led to an increase in activity of the catalyst through increasing the metal–carbon reactivity. PE with broader PDI was obtained with the catalyst B.

References

1. Britovsek GJP, Gibson VC, Wass DF (1999) Angew Chem Int Ed 38:428
2. Ittel SD, Johnson LK, Brookhart M (2000) Chem Rev 100:1169
3. Mecking S (2001) Angew Chem Int Ed 40:534
4. Britovsek GJP, Gibson VC, Kimberley BS, Maddox PJ, McTavish SJ, Solan GA, White AJP, Williams DJJ (1998) Chem Commun 7:849
5. Small BL, Brookhart M, Bennett AMA (1998) J Am Chem Soc 120:4049
6. Britovsek GJP, Dorer BA, Gibson VC, Kimberley BS, Solan GA (1999) World Pat WO 99/12981 (BP Chemicals Ltd.).
7. Gibson VC, Wass DF (1999) Chem Br 35:20
8. Johnson LK, Killian CM, Brookhart M (1995) J Am Chem Soc 117:6414
9. Johnson LK, Killian CM, Brookhart M (1995) J Am Chem Soc 118:267
10. Blum ME, Folli C, Doring M (2004) J Mol Catal A: Chem 212:13
11. Amort C, Malaun M, Krajete A, Kopacka H, Wurst K, Christ M, Lilge D, Kristen MO, Bildstein B (2002) Appl Organomet Chem 16:505
12. Ma Z, Wang H, Qiu J, Xu D, Hu Y (2001) Macromol Rapid Commun 22:1280
13. A.M.A. Bennett, (E.I. Du Pont de Nemours and Co., USA) WO9827124, 1998. [CAN 129:122973].
14. McTavish S, Britovsek GJP, Smit TM, Gibson VC, White AJP, Williams DJ (2007) J Mol Catal A: Chem 261:293
15. Ionkin AS, Marshall WJ, Adelman DJ, Shoe AL, Spence RE, Xie T (2006) J Polym Sci A Polym Chem 44:2615
16. Damavandi S, Galland GB, Zohuri GH, Sandaroos R (2011) J Polym Res 18:1059–1065
17. Zohuri GH, Damavandi S, Sandaroos R, Ahmadjo S (2011) Polym Bull 66:1051
18. Zohuri GH, Seyedi SM, Sandaroos R, Damavandi S, Mohammadi A (2010) Catal Lett 140:160
19. Rieger BL, Saunders BL, Kacker S, Striegler S (2003) (Eds.) Late Transition Metal Polymerization Catalysis, Wiley-VCH, Weinheim.
20. Ahmadjo S, Zohuri GH, Damavandi S, Sandaroos R (2010) Reac Kinet Mech Cat 101:429
21. Frisch MJ et al (2003) Gaussian 03. Gaussian, Inc., Pittsburgh