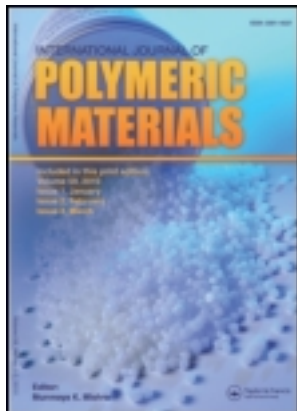


This article was downloaded by: [Institutional Subscription Access]

On: 11 September 2011, At: 01:03

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpom20>

Late Transition Metal Catalyst Based on Cobalt for Polymerization of Ethylene

G. H. Zohuri^a, S. Damavandi^b, E. Dianat^a, R. Sandaroos^c & S. Ahmadjo^d

^a Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

^b Department of Chemistry, Islamic Azad University, Sarvestan Branch, Sarvestan, Iran

^c Department of Chemistry, Faculty of Science, Birjand University, Birjand, Iran

^d Department of Catalyst, Iran Polymer and Petrochemical Institute, Tehran, Iran

Available online: 26 Jul 2011

To cite this article: G. H. Zohuri, S. Damavandi, E. Dianat, R. Sandaroos & S. Ahmadjo (2011): Late Transition Metal Catalyst Based on Cobalt for Polymerization of Ethylene, International Journal of Polymeric Materials, 60:10, 776-786

To link to this article: <http://dx.doi.org/10.1080/00914037.2010.551362>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan, sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Late Transition Metal Catalyst Based on Cobalt for Polymerization of Ethylene

G. H. Zohuri,¹ S. Damavandi,² E. Dianat,¹ R. Sandaroos,³ and S. Ahmadjo⁴

¹Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

²Department of Chemistry, Islamic Azad University, Sarvestan Branch, Sarvestan, Iran

³Department of Chemistry, Faculty of Science, Birjand University, Birjand, Iran

⁴Department of Catalyst, Iran Polymer and Petrochemical Institute, Tehran, Iran

The late transition metal catalyst of [2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride was prepared under controlled conditions and used for polymerization of ethylene. Methylaluminoxane (MAO) and triisobutylaluminum (TIBA) were used as a cocatalyst and a scavenger, respectively. The highest activity of the catalyst was obtained at about 30°C; the activity decreased with increasing temperature. At polymerization temperatures higher than 50°C not only was a sharp decrease in the activity observed but also low molecular weight polyethylene product that was oily in appearance was obtained. The polymerization activity increased with increasing both of the monomer pressure and [MAO]:[Co] ratio. However, fouling of the reactor was strongly increased with increasing both of the monomer pressure and the amount of MAO used for the homogeneous polymerization. Hydrogen was used as the chain transfer. The activity of the catalyst and the viscosity average molecular weight (M_v) of the polymer obtained were not sensitive to hydrogen concentration. However, the viscosity average molecular weight of the polymer decreased with the monomer pressure. The (M_v), the melting point, and the crystallinity of the resulting polymer at the monomer pressure of 1 bar and polymerization temperature of 20°C were 1.2×10^5 , 133°C, and 67%, respectively. Heterogeneous polymerization of ethylene using the catalyst and

Received 19 August 2010; accepted 27 December 2010.

Address correspondence to G. H. Zohuri, Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran. E-mail: GZohuri@ippi.ac.ir, and S. Damavandi, Department of Chemistry, Islamic Azad University, Sarvestan Branch, Sarvestan, Iran. E-mail: Saman_Damavandi@yahoo.com

the MAO/SiO₂ improved morphology of the resulting polymer; however, the activity of the catalyst was also decreased. Fouling of the reactor was eliminated using the supported catalyst system.

Keywords ethylene polymerization, late transition metal catalyst, olefin polymerization, slurry polymerization

INTRODUCTION

The interest in polymerization of olefins has increased recently due to the observed catalytic activity of Schiff base complexes in synthesis of commercially important polymers [1–10]. The Schiff base complexes of transition metal ions are efficient catalysts in both homogeneous and heterogeneous reactions. Activity of these complexes varied with the type of ligands used [11].

The iron(II) and cobalt(II) complexes of pyridine bis(imine) ligands showed significant activity in the polymerization of ethylene. These catalysts were also successfully used for copolymerization of ethylene and 1-hexene [12]. Early transition metal-based Ziegler catalysts and metallocenes are, unfortunately, highly sensitive to polar reagents [13]. By comparison, the late transition metal complexes are generally much more functional group tolerant due to their more oxophilic nature [13,14].

However, the late transition metal catalysts usually yield dimers or oligomers because of the propensity of alkyl complexes of the metals for chain transfer by β -hydride elimination [5,15]. The molecular weight of the produced polymer is controlled by both electronic and steric properties imparted by the bi- or tridentate ligands [14]. A key feature enabling polymerization to occur to very high molecular weight is retardation of chain transfer by the sterically bulky nature of the *o*-aryl substitution. Brookhart and his co-workers reported interesting results in the late transition metal olefin polymerization catalysis and spurred an intense research for suitable ligand structures [14]. The polymerization reaction is expected to be cationic due to the cationic nature of the metal. Subsequently, three different research groups (Brookhart, Gibson, and Bennett of Dupont) independently reported cationic iron and cobalt catalyst systems for the polymerization of ethylene to high linear high crystalline high density polyethylene [3,16–19].

The late transition metal catalysts are usually supported on inorganic or polymeric materials [20,21]. Among the suitable supports, inorganic oxides of silica and MgCl₂ seem to be particularly effective. The supported catalysts produce better morphology of the polymer with lower fouling of the polymerization reactor [21–23].

Previously, we found that molecular weight of the polymer produced is strongly affected by the steric bulky group of *o*-aryl substitution [24]. In this study, [2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II)

dichloride was prepared as a late transition metal catalyst. The bulkier group substitutions (isopropyl) can enhance the activity that has been reported [25–28]. Ethylene polymerization was carried out with the prepared catalyst and the effects of the polymerization temperature, cocatalyst/catalyst molar ratio, monomer pressure, and polymerization time were investigated. Influence of hydrogen concentration on the polymerization activity and the viscosity average molecular weight were investigated. Heterogeneous polymerization was also designed and used for the polymerization. Morphology and some specifications of the resulting polymer were studied.

EXPERIMENTAL

Tetrahydrofuran, chloroform, methanol, 4-toluenesulfonic acid, and 2,6-diisopropylaniline 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). Methylaluminoxane (MAO) (10% solution in toluene), triisobutylaluminum (TIBA) (purity 93%), 2,6-diacetylpyridine (purity >99%), and CoCl₂ were purchased from Sigma Aldrich Chemicals (Steinheim, Germany). SiO₂ (PQ 3050) was supplied from PQ Corporation (USA). The chemical was calcined at about 400°C for 5 hours before use. Polymerization of ethylene at low pressure was carried out in a three-necked glass reactor, while higher pressure polymerization was carried out in a 1 L, stainless-steel Buchi reactor (bcp 250) equipped with controllers systems as previously described [29]. Methanol was used as antisolvent.

Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10°C/min instrument was 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. The viscosity average molecular weight (M_v) and crystallinity of some polymer samples were determined according to the literature [29,30]. Calculation of $H_f/H_f^* \times 100$ gives the values of crystallinity where H_f is the heat of fusion and $H_f^* = 69$ 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 $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$. All the catalyst preparation and polymerization procedures were carried out under dried N₂. ¹H NMR spectrum was recorded on a Bruker BRX-100

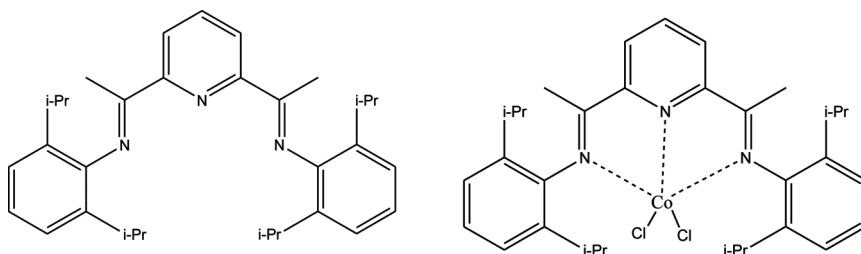


Figure 1: Structures of the ligand and the catalyst.

AVANCE spectrometer. The peak melting temperature (T_m) of the polymers was determined by DCS (Universal V4IDTA) while reheating the polymer sample to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$. Elemental analysis for CHN was carried out by CHNO type Thermo Firingan 11112EA microanalyzer. The scanning electron microscopic (SEM) images were recorded on a LEO 1530 FEGSEM microscope.

Ligand Preparation

To a solution of 2,6-diacetylpyridine (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, when a white precipitate had formed. The precipitate was filtered, washed with cold methanol, and dried. A pale yellow solid was obtained. ^1H NMR study revealed that both the monoamine and diimine products were present. Therefore, the resulting solid was dissolved in a boiling mixture of methanol and chloroform. Addition of chloroform was continued until the solid was dissolved following excess addition of 2,6-diisopropylaniline (6.1 mmol, 1.19 ml). The solution was refluxed for 5 days. The solvent was removed, and a yellow solid was obtained that was washed with n-hexane and dried (67% yield). Figure 1 shows the structure of the ligand [2,6-Diacetylpyridinebis(2,6-diisopropylphenylimine)]. ^1H 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. ($\text{C}_{33}\text{H}_{43}\text{N}_3$) calcd: C, 82.32; H, 8.94; N, 8.73. Found: C = 82.33%, H = 9.11%, and N = 8.68%.

Catalyst Preparation

In a dry, oxygen-free atmosphere, CoCl_2 (anhydrous, 1.078 mmol, 0.14 g) was dissolved in dry THF. [2,6-Diacetylpyridinebis(2,6-diisopropylphenylimine)], the ligand, (1.156 mmol, 0.46 g) was added. The mixture was stirred for 3 days at room temperature; a brown precipitate was formed. The solid product was filtered, washed with dry n-hexane, and dried under N_2 . The solid catalyst of [2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride

(yield 76%) was obtained (Figure 1). $^1\text{H NMR}$ (CD_2Cl_2): δ 114.91 (2H, Py- H_m), 5149.85 (1H, Py- H_p), 10.01 (4H, Ar- H_m), 4.41 (6H, NdCCH₃), -8.88 (2H, Ar- H_p), -16.74 (12H, *iPr-Me*), -18.22 (12H, *iPr-Me*), -81.92 (6H, *iPr-CH*).

RESULTS AND DISCUSSION

The activity of the catalyst, R_p (average) is expressed as g PE/(mmol Co. h), which was determined after 60 min of the polymerization for each run. It should be noted that due to the homogeneous nature of the catalyst system employed, fouling was observed even at the low pressure of the polymerization. Upon the addition of the catalyst components, a change in the color of the catalyst solution to blue was observed. This is probably due to the alkylation and the formation of the active Co-C bond. It has been reported that alkylation is not the rate-limiting step in a chain propagation reaction [31].

The polymerization was studied at various concentrations of MAO while concentration of the catalyst, the monomer pressure, stirrer speed, and the polymerization temperature were kept constant. The polymerization activity increased linearly with the addition of the [MAO]:[Co] ratio (Figure 2). Due to the oligomeric nature of the MAO, the chemical is not able to deactivate or overreduce the catalyst active centers, even at high concentration [24]. Increasing the [MAO]:[Co] ratio up to 7500:1 produced some oily form polyethylene. However, only the precipitated polymer has been reported as the product, so a slightly decay which was observed in the Figure 2 at the [MAO]:[Co] ratio up to 7500:1 could be the result of relinquishing of the oily form of the polymer produced. The oily form of polyethylene could have been produced by the excessive chain transfer reactions due to the very high levels of MAO present.

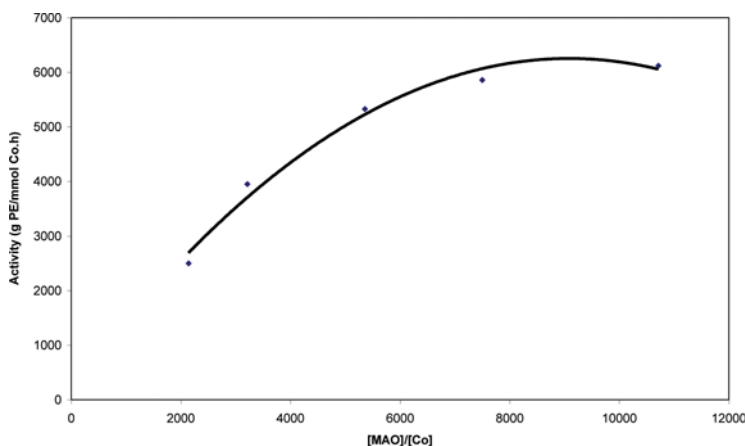


Figure 2: Effect of MAO concentration on the average rate of polymerization. Polymerization conditions: Temperature = 20°C, Time = 60 min, Pressure = 1 bar, (Co) = 0.9×10^{-3} mmol, Toluene = 50 ml.

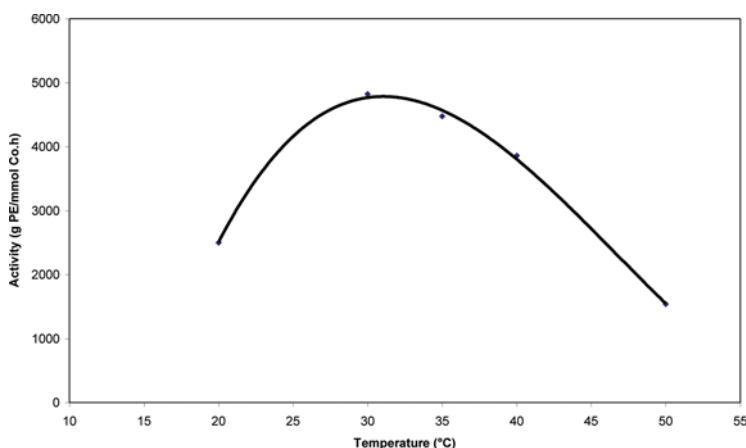


Figure 3: Effect of temperature on the average rate of polymerization. Polymerization conditions: Time = 60 min, Pressure = 1 bar, (Al):(Co) = 2140:1, (Co) = 0.9×10^{-3} mmol, Toluene = 50 ml.

The polymerization reactions were carried out at the temperature between 20 and 60°C. The highest activity of the catalyst was obtained at about 30°C. The catalyst activity increased from 20°C to 30°C. Further increase in temperature led to a dramatic decline in activity, as can be seen in Figure 3. An increase in the values of the propagation rate constant with increasing the temperature and irreversible deactivation of the active sites at high temperature was reported [32–34]. Higher temperature supplies the activation energy needed for chain transfer reactions, especially β -hydride elimination [35]. As higher temperatures increase the diffusion of the monomer to the active centers, the increase in temperature also reduces the solubility of the ethylene gas in the solvent [36–38]. The opposing effects led to the observations of rate change with temperature. These behaviors were confirmed with the trending in M_v of the resulting polymer (Table 1). At temperatures higher than 50°C, not only the activity of the catalyst decreased, but also a low molecular weight oily polyethylene was produced through β -hydride elimination.

Table 1: Characterization of the resulting polymer

Pressure (bar)	H ₂ (ml)	Temperature (°C)	ΔH Cry	Crystallinity %	T _m (°C)	\overline{M}_v
0.5	–	30	40.70	66.6	132	–
1	–	20	40.87	67	134	1.2×10^5
3	–	30	28.63	47	131	1.1×10^5
5	–	30	25.9	42	130	0.8×10^5
0.5	20	30	40.53	66	131	–
0.5	40	30	40.19	65	132	–
1	–	40	39.11	63	129	2.8×10^4
1	–	50	35.76	58	129	2.3×10^4

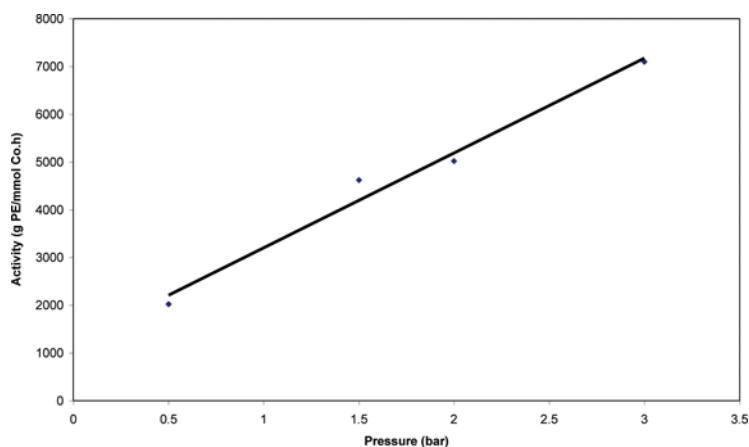


Figure 4: Effect of monomer pressure on the polymerization behavior. Polymerization conditions: Toluene = 50–300 ml, Temperature = 30°C. Other conditions as in Figure 3.

The influence of monomer pressure between 0.5 and 5 bar on the catalyst behavior was studied. The polymers obtained at the monomer pressure higher than 3 bars were coated on the reactor walls and the fouling was remarkably high. The polymerization behavior is shown in Figure 4. The polymerization reactions were carried out using $[Al]:[Co] = 2140:1$ and the optimum temperature previously established. The higher the pressure of the monomer, the higher the activity of the catalyst observed. The behavior is mainly due to high concentration of the monomer close to the catalyst active centers.

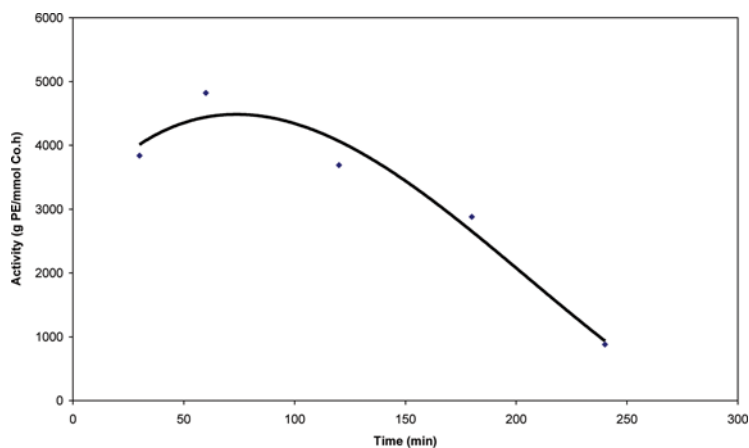


Figure 5: Plot of R_p versus time. Polymerization conditions: Temperature = 30°C, Pressure = 1 bar, $[Al]:[Co] = 2140:1$, $[Co] = 0.9 \times 10^{-3}$ mmol, Toluene = 50 ml.

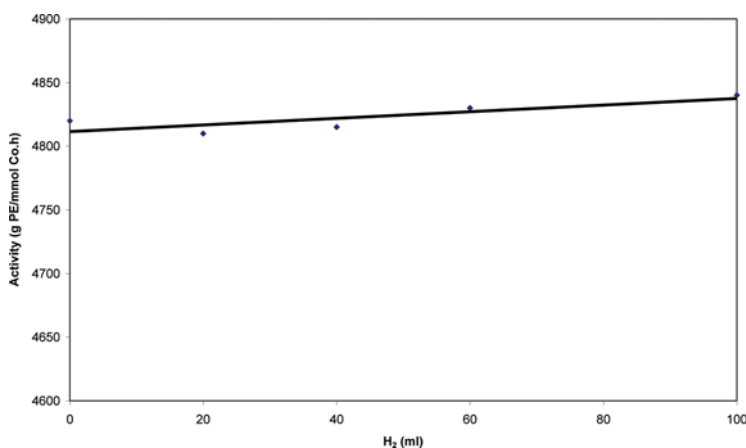


Figure 6: Influence of the hydrogen concentration on the polymerization activity. Polymerization conditions as in Figure 4.

It should be noted that fouling was observed even at low monomer pressure, which is due to the homogeneous nature of the polymerization. Fouling of the reactor was increased with increasing pressure of the monomer and MAO concentration. A dramatic effect on the crystallinity of the resulting polymer was observed with increasing of the monomer pressure. The crystallinity of the polymer at the monomer pressures of 1, 3, and 5 bars were 67, 47, and 42%, respectively (Table 1). At lower pressure due to the existence of bulky substitutions that block the axial position for monomer transferring, monomer insertion is favored, resulting in the formation of almost linear and semicrystalline polyethylene. However, at higher pressure, in spite of the existence of sterically bulky substitutions, probable chain transfer reactions to the

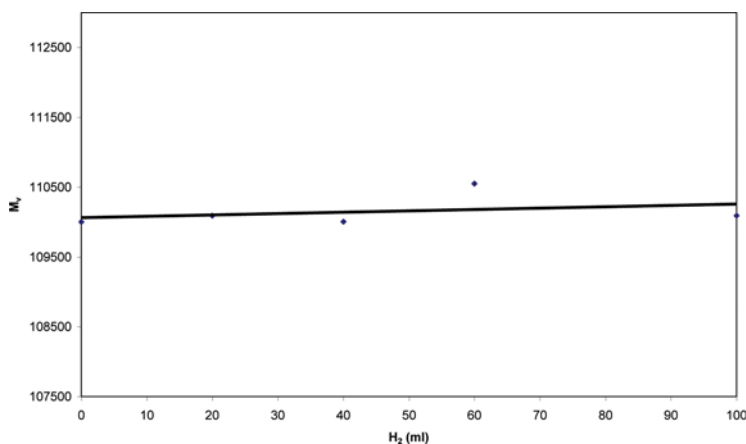


Figure 7: Influence of the hydrogen concentration on the \overline{M}_n of the polymer obtained. Polymerization conditions as in Figure 4.

Table 2: Characterization of the resulting polymer

Polymerization	Temperature (°C)	Pressure (bar)	Activity (g PE/mmol Co. h)
Homogeneous	30	1	4820
Heterogeneous	30	1	3240

monomer resulted in the formation of fewer branches due to re-insertion of oligomers terminated via β -H elimination, which are still capable of being coordinated to the active centers.

Figure 5 shows the average rate of polymerization versus reaction time. The maximum activity of the catalyst was observed after 60 min of the polymerization for the reaction carried out at 30°C.

Hydrogen was used as a chain transfer agent while the polymerization was carried out at the optimum conditions established before. The activity of the catalyst and the viscosity average molecular weight of the polymer obtained were not sensitive to the amount of hydrogen concentration (Figures 6 and 7). However, at higher concentration of hydrogen the catalyst activity can increase slightly. 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 [38].

Homogeneous polymerization produced a polymer with irregular shape and size with some dusty particles causing fouling of the reactor. Heterogeneous polymerization improved morphology of the polymer particles. However, it decreased the activity of the catalyst (Table 2). Elimination of the dusty particles due to heterogeneous polymerization diminished fouling of the reactor.

CONCLUSION

The following results were obtained using the homogeneous [2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride catalyst for polymerization of ethylene.

1. The prepared catalyst of [2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride was an active catalyst for the ethylene polymerization.
2. Polymerization reactions were carried out between 20 and 65°C. The optimum activity of the catalyst was obtained at 30°C. At temperatures higher than 50°C a completely oily, low molecular weight polymer was obtained.
3. Polymerization activity was increased with increasing both of the monomer pressure and [MAO]/[Co] ratio, at the expense of increased reactor fouling.

4. The viscosity average molecular weight of the resulting polymer decreased with increasing of the monomer pressure.
5. The polymerization reactions were carried out at different levels of hydrogen. Neither the activity of the catalyst nor the viscosity average molecular weight (\overline{M}_v) of the polymer obtained were affected by the hydrogen concentration.
6. The polymer obtained has high crystallinity of about 67% that is comparable with the polymer obtained using Ziegler-Natta or metallocene catalysts. However, increasing of the monomer pressure reduced the crystallinity of the polyethylene obtained.
7. A viscosity average molecular weight (\overline{M}) of 1.2×10^5 was achieved for the polymer obtained at 20°C temperature and the monomer pressure of 1 bar. However, at higher temperatures up to 50°C, the \overline{M}_v was decreased to 2.3×10^4 .
8. Heterogeneous polymerization decreased the activity of the catalyst, improved morphology of the resulting polymer, and eliminated fouling of the polymerization reactor.

REFERENCES

- [1] Plentz-Menghetti, S.; Kress, J.; Lutz, P. J. *Macromol. Chem. Phys.* **2000**, *201*, 1832.
- [2] Small, B. L.; Brookhart, M. *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.* **1998**, *39*, 213.
- [3] Young, M.-J.; Ma, C.-C. *Polym. Plastics Tech. and Eng.* **2002**, *41*, 601.
- [4] Rabagliati, F.M.; Terraza, C.A.; Quijada, R. *Int. J. Polym. Mat.* **2009**, *58*, 202.
- [5] Shantilal, B.O.; Naved, I.M.; Ashesh, K.P. *Int. J. Polym. Mat.* **1996**, *34*, 163.
- [6] Mekewi, M.A. *Int. J. Polym. Mat.* **2005**, *55*, 210.
- [7] Guessoum, M.; Haddaoui, N.; Fenouillot, F. *Int. J. Polym. Mat.* **2008**, *57*, 657.
- [8] Shang, X.-Y.; Fu, X.; Yang, L.-S.; Chen, X.-D.; Zhang, M. *Int. J. Polym. Mat.* **2008**, *57*, 362.
- [9] Elaine, V.D.G.; Clara, M.; Oliveira, F.; Marcos, L.D. *Int. J. Polym. Mat.* **2008**, *57*, 675.
- [10] Murugesan, V.; Umapathy, M. J. *Int. J. Polym. Mat.* **2010**, *59*, 647.
- [11] Britovsek, G.J.P.; Gibson, V.C.; Kimberley, B.S.; Maddox, P.J.; McTavish, G.A.; Solan, G.A.; White, A.J.P.; Williams, D.J. *Chem. Commun.* **1998**, 849.
- [12] Li, B.; Qingfeng, W.; Zhou, N.; Shi, B. *Int. J. Polym. Mat.* **2011**, *60*, 51.
- [13] Britovsek, G.J.P.; Gibson, V.C.; Kimberley, B.S.; Mastroianni, S.; Red-Shaw, C.; Solan, G.A.; White, A.J.P. *Dalton Trans.* **2001**, 1639.
- [14] Murugesan, V.; Umapathy, M.J. *Int. J. Polym. Mat.* **2010**, *59*, 647.

- [15] Ni, P.; Thring, R. *Int. J. Polym. Mat.* **2003**, *52*, 685.
- [16] Mecking, S. *Angew. Chem. Int. Ed.* **2001**, *3*, 40.
- [17] Wilke, G. *Angew. Chem.* **1998**, *100*, 189.
- [18] Brookhart, M.; Preishuber-Pflugl, P. *Macromolecules* **2002**, *35*, 6074.
- [19] Bennett, A.M.A. Dupont WO 98 27124, **1998**.
- [20] Britovsek, G.J.P.; Mastroianni, S.; Solan, G.A.; Baugh, S.P.D.; Redshaw, C.; Gibson, V.C.; White, A.J.P.; Williams, D.J.; Elsegood, M.R.J. *Chem. Eur. J.* **2000**, *6*, 2221.
- [21] Liu, Y.-L.; Xu, J.-T.; Dong, Q.; Fu, Z.-S.; Fan, Z.-Q. *Polym. Plastics Tech. and Eng.* **2009**, *48*, 333.
- [22] Ye, L.; Haijing, R.; Zhaokun, L. *Int. J. Polym. Mat.* **2010**, *59*, 710.
- [23] Wang, J.; Wang, L.; Wang, W.; Chen, T.; Wang, W.; Sun, T.; Feng, L.; Gao, H. *Polym. Plastics Tech. and Eng.* **2006**, *45*, 1053.
- [24] Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377.
- [25] Xu, R.; Liu, D.; Wang, S.; Mao, B. *Macromol. Chem. Phys.* **2006**, *207*, 779.
- [26] Mahdavi, H.; Badiei, A.; Zohuri, G.H.; Rezaee, A.; Jamjah, R.; Ahmadjo, S. *J. Appl. Polym. Sci.* **2007**, *130*, 1517.
- [27] Meurs, M.V.; Britovsek, G.J.P.; Gibson, V.C.; Cohen, S.A. *J. Am. Chem. Soc.* **2005**, *127*, 9913.
- [28] Popeney, C.; Guan, Z. *Organometallics* **2005**, *24*, 1145.
- [29] Salo, E.V.; Guan, Z. *Organometallics* **2003**, *22*, 5033.
- [30] Silver, J.; Zakrzewski, J.; Tosik, A.; Bukowska-Strzyzewska, M. *J. Organomet. Chem.* **1997**, *540*, 169.
- [31] Zohuri, G.H.; Azimfar, F.; Jamjah, R.; Ahmadjo, S. *J. Appl. Polym. Sci.* **2003**, *89*, 1177.
- [32] Peacock, A. *Handbook of Polyethylene: Structures, Properties, and Applications*; Marcel Dekker, Inc.: New York, 2000, 57.
- [33] Busico, V.; Talarico, G.; Cipullo, R. *Macromol. Symp.* **2005**, *226*, 1.
- [34] Jochem, T.M.P.; Wickert, G.; Wim, P.M.S. *Chem. Eng. Sci.* **2002**, *57*, 3461.
- [35] Moor, E.P. *Polypropylene Handbook*; Hanser Publishing: Munich, 1996.
- [36] Salamone, J.C. *Polymeric Materials Encyclopedia*, Vols. 6, 8, 10; CRC Press: Boca Raton, FL, 1996, 4727–4739.
- [37] Deck, P.A.; Bewick, C.L.; Marks, T.J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.
- [38] Justino, J.; Romano, D.A.; Ascenso, J.; Marcues, M.; Tait, P.J.T. *Polym. Int.* **1997**, *44*, 407.
- [39] Rieger, B.L.; Saunders, B.L.; Kacker, S.; Striegler, S., Eds. *Late Transition Metal Polymerization Catalysis*; Wiley-VCH: Weinheim, 2003.