Bis(Imino) Pyridyl Iron Complexes: the Effect of Polymerization Conditions on Activities and Thermal Behaviors of Polyethylene

Ali Ghotbi Taheri[1], Saeid Ahmadjo[2]*, Golam Hossein Zohuri[1], Saman Damavandi[3], Mahdi Mortazavi[2], and Samaneh Dehgani[1]

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

[2] Department of Catalyst, Iran Polymer and Petrochemical Institute (IPPI), Tehran, Iran

[3] Rejal Petrochemical Company Isfahan, Bldg Negin Zayandeh Rod, Moshtagh Street, Isfahan, Iran

ABSTRACT

Two late transition metal catalysts based on 2,6-bis(imino)pyridine iron(II) were synthesized by introducing methyl substitution (catalyst A) and *t*-Butyl substitution (catalyst B) at the *ortho* position of the aryl rings of the ligand. Comparative ethylene polymerizations using the catalysts showed quiet different behaviors. The activity of catalyst A was higher than that of catalyst B in all of the polymerization conditions used. The highest activities of these catalysts were obtained at almost 25°C. Activities of the catalysts increased with increasing both monomer pressure and [Al]: [Fe] molar ratio. Multi modal peaks were appeared in the DSC analysis of oligomers obtained by catalyst A, while in the DSC analysis of the polymer obtained using catalyst B unimodal peaks were appeared. It is suggested that catalyst A containing less bulkier substitution produced polymer with different molecular weight fractions and different melting points. Besides, the t-butyl group in catalyst B resulted in producing polyethylene (PE) with single sharp DSC peaks; the latter is due to the formation of highly linear polyethylene. Polymerization temperatures affected the pattern of DSC thermograms in terms of number and shape of the peaks of the obtained polymers by catalyst A. Catalyst A produced linear oligomers contained liner olefinic part with a number average molecular weight in the range of 260 to 361.

Keywords: Polyethylene, Late Transition Metal, Fe-based Catalyst, Polymerization, Bis(Imino)Pyridine

INTRODUCTION

Since the pioneering work by Karl Ziegler and Giulio Natta in the early 1950's on the polymerization of simple olefins, there has been intense interest in the application of early transition metal catalysts for the selective polymerization of inexpensive olefins. Following to the Ziegler-Natta catalysts metallocene catalysts were discovered in the late 1980's and resulted in numerous industrial processes for improving the properties of polyolefinic materials along with performance parameters. This field has been remarkably renewed with the use of catalysts based on early transition metals [1, 2]. In the past, late transition metal catalysts were generally accepted for producing oligomers because of the accelerated β-hydride elimination as a chain transfer reaction [3]. However, in 1995 Brookhart and co-workers turned a new page in the research on transition metal complex catalysts when they announced novel nickel- and
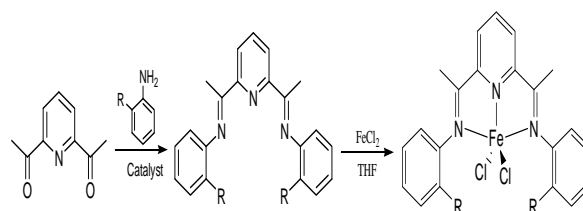
palladium-based polymerization catalyst precursors [4]. The aim of the research was the same as in single site metallocene studies to understand the relation between catalyst structure and polymer micro structure so as to improve catalyst performance. These catalysts are exclusive in the polymerization of ethylene to give a variety of materials, ranging from highly viscous liquids to rubbery elastomeric materials and to rigid linear polyethylenes [4-6]. Brookhart, Bennet [7,8], and Gibson [9] independently discovered that five coordinate 2,6-bis(imino)pyridine Fe(II) and Co (II) dihalides, activated with MAO, made effective catalysts for the conversion of ethylene either to high density polyethylene or to oligomers contain linear α-olefins. Remarkably the activities were as high as those of most efficient metallocene catalysts [5-11].

Many studies have been directed towards introducing functional groups or alkyl substitutions to the imine nitrogen donors of the ligand. Bennett and co-workers reported an imidazolyl substituted derivative that showed similar activity to its ketimine analogue [12]. Gibson and co-workers studied systematic variations at the imine carbon position [13]. Ionkin and co-workers investigated ethylene polymerization using a series of nitro-substituted bis (imino)pyridine complexes based on iron [14].

Our researches focused on the relationship between structures and activities of the catalysts as well as the stability of the obtained polymer and catalysts life time during the polymerization of ethylene [15-17]. In this work, we report the synthesis, characterization, and ethylene poly merization of two bis(imino)pyridine catalysts, containing different substituents with respect to the steric properties at the ortho position of the aryl rings (Scheme 1). The replacement of ortho substitution from Me (methyl) to t-Bu (t-Butyl) is expected to obtain significant change in steric bulkiness of the catalyst, which results in noticeable alteration in catalyst activities and polymer properties. Although many bis(imino)pyridine catalysts have been

tried out for ethylene polymerization and data for activities have been reported [18-22], less attention has been paid to the catalyst behaviors during the polymerization and to the thermal behaviors of the resulting polymers. Thus, the investigation of the catalysts behaviors during the polymerization using these catalysts and the thermal behaviors of the obtained polymers would be highly desirable.

Scheme 1: Synthesis of catalysts A and B (catalyst A: R=Me; catalyst B: R=t-Bu).

EXPERIMENTAL PROCEDURES

All manipulation was carried out under an atmosphere of nitrogen using standard Schlenk technique or in a conventional glove box. Dichloromethane, methanol, ethanol, benzene, and iron dichloride were supplied by Merck Chemical (Darmstadt, Germany) and were used as received. Tetrahydrofuran and toluene (Merck Chemical) were prepared from distilling over sodium wire, benzophenon, and calcium hydride respectively. The chemicals were stored over sodium wire and 13X and 4 Å activated molecular sieves. Nitrogen (purity 99.99%) was supplied by Roham (Tehran, Iran). Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical (Tehran, Iran). The gases were purified as explained elsewhere [23]. Aniline derivatives were supplied by Merck Chemical and vacuum-distilled before use. 2, 6-Diacetylpyridine (purity > 99%) was prepared from Acros (Somerville, NJ). Methylaluminoxane (MAO) (10% solution in toluene) was prepared by Aldrich Chemical (Steinheim, Germany). Catalyst component handling and polymerization procedures were carried out as previously described [24]. Solvent were refluxed over an appropriate drying agent and distilled and degassed prior to use. Differential

**Journal of Petroleum
Science and Technology**

A. Ghotbi Taheri, S. Ahmadjo, G. H. Zohuri, S. Damavandi et al.

scanning calorimetry (DSC) (Universal V4IDTA) instrument at a rate of 10°C/min was used for the 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. According to the literature, the calculation of $(\Delta H_f/ (\Delta H_f^*) \times 100$ gives the value of crystallinity, where $(\Delta H_f$ is the heat of fusion and $\Delta H_f^* = 69$ cal/g is the heat of the fusion of 100% crystalline polyethylene [15,25]. Elemental analyses for CHN were carried out by the CHNO type from the Helaus Co. ^{1}H NMR 400 MHz model Avance 400 Bruker techniques were used for structural characterization. For ^{13}C NMR study, the solutions were prepared in 1, 3, 5 - trichlorobenzene and 1, 1, 2, 2-tetrachloroethane-d (20 %vol) for an internal lock signal, and spectra were recorded at 120°C. The general procedure of the polymerization was to adding MAO (10%wt in toluene) to the reactor containing toluene (80 ml) followed by the addition of the dissolved catalyst in toluene (5 ml) solution. The reactor was previously purged with nitrogen for 15 min following to purge with ethylene and the contents were stirred and maintained under ethylene during the course of the polymerization. The solid polyethylene was collected by filtration, washed with acidic methanol (50 ml), and dried (in a vacuum oven at 35°C).

Preparations of 2, 6-Bis (Imino) Pyridine Ligands2, 6-Diacetylpyridine Bis (2-Dimethylanil) (Ligand A)

To a solution of 2, 6-diacetylpyridine (0.75 gr, 4.6 mmol) in dichloromethane (12.5 ml), *ortho* toluidine (0.985 ml, 9.2 mmol) was added. Formic acid (97%, 2–3 drops) was added to reach a pH of 4–6, and the solution was refluxed overnight. Upon cooling to room temperature, the solvent was evaporated, and the product was crystallized from ethanol. After filtration, the yellow solid was washed with cold ethanol and dried in a vacuum oven (50°C) overnight to produce 2,6-diacetylpyridinebis(2-dimethylanil) (1.66 gr, the yield was 55%).

($C_{23}H_{23}N_3$) ^{1}H NMR (CDCl$_3$) analysis: δ = 8.42 (d, Py-m-H), 7.91 (t, Py-p-H), 7.24 (m, Aryl), 7.07 (t, Aryl), 6.70 (d, Aryl), 2.36 (s, N=C-CH$_3$), 2.14 (s, Aryl CH$_3$).

Elemental analysis: Calculated (%): C =80.90, H= 6.79, N =12.31; found (%): C= 80.35, H= 6.77, N=12.11.

Diacetylpyridine bis(2-tert-butylanil) (ligand B)

To a solution of 2, 6-diacetylpyridine (1.55, 9.5 mmol) in dichloromethane (20 ml), 2-tert-butylaniline (3 ml, 19 mmol) was added. By using the procedure described previously, the ligand as a yellow powder was obtained (60% yield).

($C_{29}H_{35}N_3$) ^{1}H NMR (CDCl$_3$) analysis: δ = 8.4 (d, 2H, Py-m-H), 7.9 (t, 1H, Py-p-H), 7.24-7.44 (m, 8H, Ar-H), 6.70 (d, Aryl), 2.36 (s, 6H, N=C-CH$_3$), 2.14 (s, 18H, CH3.)

Elemental analysis: Calculated (%): C =81.84, H= 8.29, N =9.87; found (%): C= 81.35, H= 8.21, N=9.67.

Catalysts Preparation

Diacetylpyridine Bis (2-Dimethylanil) Iron (II) Dichloride (Catalyst A)

Catalyst A was prepared using equal molar chemicals of ligand A and anhydrous iron dichloride compounds. The ligand (0.3 gr) and anhydrous iron dichloride (0.2 gr) were mixed using a 50 ml flask containing THF (15 ml) under dried Ar gas. The content of the flask was stirred for 30 min. The solvent was evaporated using a vacuum oven. The solid catalyst (0.48 gr) was obtained, and the product was blue powder, which was subsequently washed with dried diethyl ether (3 × 10 ml), filtered, and dried.

Diacetylpyridine Bis (2-Tert-Butylanil) Iron (II) Dichloride (Catalyst B)

The procedure used for the preparation of catalyst A was repeated with 2, 6-diacetylpyridinebis (2-tert-butylanil) (ligand B) and anhydrous iron dichloride compounds. The product was a blue powder compound.

RESULTS AND DISCUSSION

The activities of the catalysts are expressed as kg PE/ (mol Fe.hr), which were determined after 30 min of polymerization for each run; the polymerizations were also studied at a constant concentration of the catalyst. Figure 1 shows the effect of [Al]: [Fe] molar ratio on the activity of the catalysts. The molar ratios from [Al]: [Fe] = 600:1 to about [Al]:[Fe] = 1500:1 increased the activities of both catalysts; however, beyond this ratio the activities slightly increased in the range studied for both catalysts. This behavior is common for the catalysts such as metallocene and late transition metal catalysts activated with MAO as the cocatalyst [10, 15-17]. Because of the oligomeric nature of the MAO, the chemical is not able to deactivate or over reduce the catalytic active centers even at a very high concentration [11, 26]. The steric properties of the 2, 6-*ortho* positions of the N-aryl groups are distinctive in determining whether the catalyst acts as a polymerization or as an oligomerization catalyst. When a single *ortho*-substituent with low steric hindrance is present [e.g. Me] on the N-aryl ligand backbone, the iron and cobalt systems majorly act as a selective oligomerization catalysts producing highly linear or branched α-olefins with a Schulz Flory distribution. However, if the catalyst *ortho*-position is hindered by sterically bulk substitution, the catalyst produces majorly a polymer product rather than an oligomer product [7-10]. The oligomers obtained by catalyst A were in a waxy-like form. However, the polymers obtained by catalyst B were in a powder-like form. It could be due to changing the substitute from methyl to *tert*-butyl. The waxy form of oligomers could be produced as a result of the excessive chain transfer reactions.The influence of the polymerization temperature on the catalytic activity has also been investigated. The polymerization was carried out at temperatures between 5 up to 65°C (Figure 2). For catalyst A, the activity reaches its maximum at about 10°C and then declines slowly by increasing the polymerization temperature.
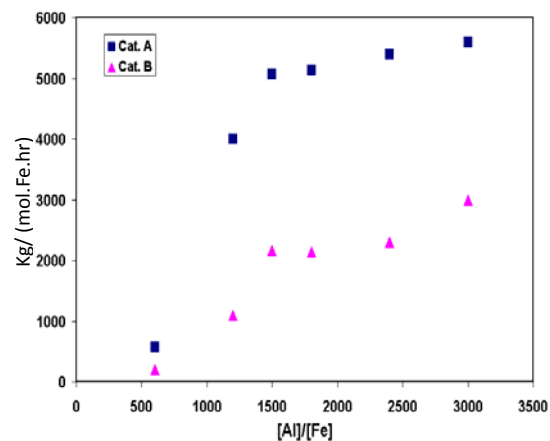

Figure 1: Effect of [Al]: [Fe] molar ratio on catalysts activities; polymerization conditions: polymerization time = 30 min, monomer pressure = 2 bar, [Fe] = 0.006 mmol, toluene = 80 ml, temperature = 26°C, and stirrer speed = 800 rpm.

In spite of the lower activity of catalyst B, a similar trend of temperature behavior was observed for both catalysts. For both catalysts, the polymerization activities vigorously decreased at temperatures higher than 55°C.

An increase in the values of the propagation rate constant with increasing the polymerization temperature and the irreversible deactivation of the active sites at a high polymerization temperature was reported [15,27]. Additionally, the higher polymerization temperature facilitates the transfer of the monomer to the catalytic active centers; meanwhile, the solubility of the monomer gas in the polymerization solvent decreased with increasing polymerization temperature and all of these effects resulted in a reduction in catalysts activities [10,17]. A significant difference in the activity of catalyst B in comparison with catalyst A was observed at 25°C (from 4000 kg PE/mol Fe.hr to 2150 kg PE/mol Fe.hr). Increasing steric bulkiness at the *ortho*-aryl position results in a decrease in activity, which was reported already [5,7,21]. The steric properties imposed by the *ortho*-aryl position were found to inhibit ethylene capture in the bulky ligands and caused an insertion restriction for monomer, which resulted in a decrease in the catalyst activity [21,22].

**Journal of Petroleum
Science and Technology**

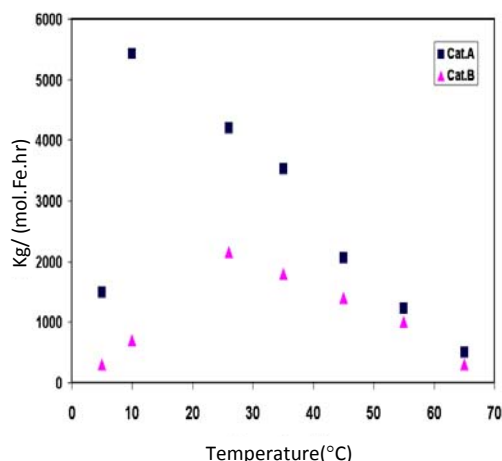A. Ghotbi Taheri, S. Ahmadjo, G. H. Zohuri, S. Damavandi et al.

Figure 2: Effect of polymerization temperatures on the catalysts activities; polymerization conditions: polymerization time = 30 min, monomer pressure = 2 bar, [Al]: [Fe] = 1500, [Fe] = 0.006 mmol, toluene = 80 ml, and stirrer speed = 800 rpm.

According to the Figure 3, the activities of the catalysts increased to a certain maximum of polymerization time. The maximum activities of the catalysts were observed after 30 min of the polymerization for the reaction carried out at 30°C; similar behavior has also been reported elsewhere [15-17]. In the early stage of the polymerization, the catalytic active centers are activated with MAO and lie easy to access the monomer, while with increasing the polymerization time the possibility of the destruction of active centers increases and leads to decreasing the catalyst activity [5,17]. This would imply that catalysts containing less sterically hindered ligands should provide easier access to the metal center and should consequently afford higher activities. However, reducing the steric protection of the metal center can lead to a more rapid decomposition of the active species [5,21]. Ethylene pressure can have an effect on the activities of the catalysts. The influence of the monomer pressure (between 1 and 8 bar) on the catalysts behaviors were studied for both catalysts. The activities of the catalysts showed nearly a linear plot versus the monomer pressure (Figure 4). The fact can be attributed to the fact that catalyst active sites were exposed to higher ethylene concentration at higher pressure.
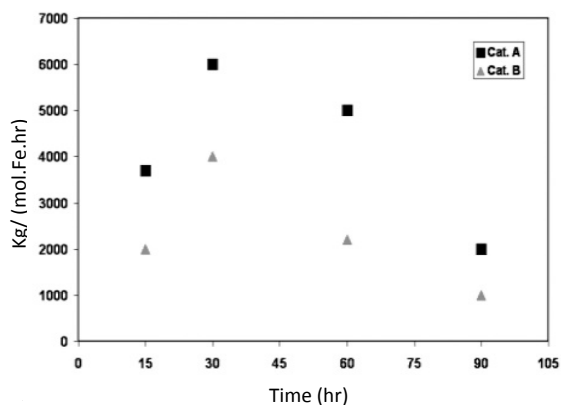

Figure 3: Effect of reaction time on the catalysts activities; polymerization conditions: temperature = 30°C, monomer Pressure = 2 bar, [Al]: [Fe] = 1500:1, [Fe] = 0.006 mmol, and toluene = 80 ml.

Polyethylene Characterization

Some characteristics of the obtained polyethylene were investigated by differential scanning calorimetry (DSC) technique. The oligomers obtained by catalyst A were waxy and showed broad and multimodal peaks on the DSC thermogram. Brookhart and Gibson reported bimodality on molecular weight for such polymers; however, the thermal behaviors for these polymers were not investigated [5-11].
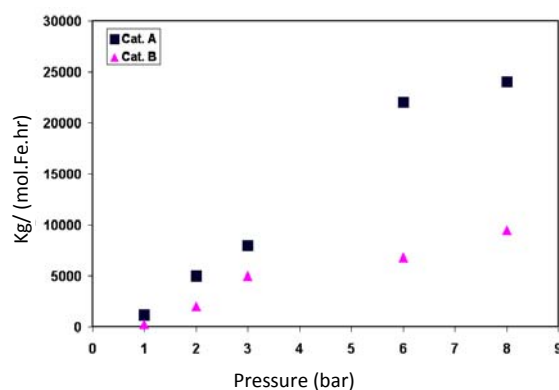

Figure 4: Effect of the monomer pressure on the catalysts activities. Polymerization conditions: toluene=80 ml, temperature = 25°C, polymerization time = 30 min, [Al]: [Fe] = 1500:1, [Fe] = 0.006 mmol, and stirrer speed = 800 rpm.

The polymers obtained by catalyst B were powder, and it seems that catalyst B produces essentially linear polyethylene because of DSC thermal peaks related to theirs melting points (all of them showed melting points between 130-135°C); however,

catalyst A produced oligomers, the thermal peaks of which were related to melting points below 100°C. Additionally, no significant change in DSC thermogram was found with increasing the molar ratio of [Al]:[Fe] from 500 to 1250 for catalyst A, while a higher ratio of [Al]:[Fe]=1500 changed the number of peaks from two to three (Figure 5). The multi modality observed for these oligomers can be due to a change in chain transfer rates or due to a difference between the molecular weights of the oligomers as reported previously [9,11,21]. The multimodality of the polymer product was reduced with increasing the polymerization temperature. The behavior was pronounced particularly at the polymerization temperature higher than 40°C, in which the number of peaks decreased to two or even one peak depending on the polymerization temperatures (Figure 6). It is presumable that the smaller chain oligomers were converted to the bigger one and the low temperature peak (observed on the 10°C) was eliminated. Scheme 2 shows a possible hypothetical for explaining this phenomenon.
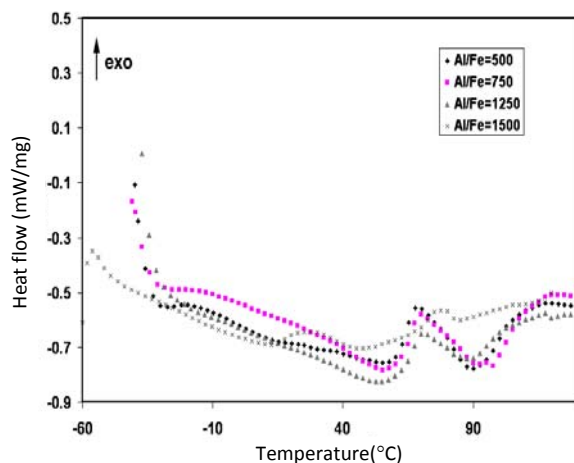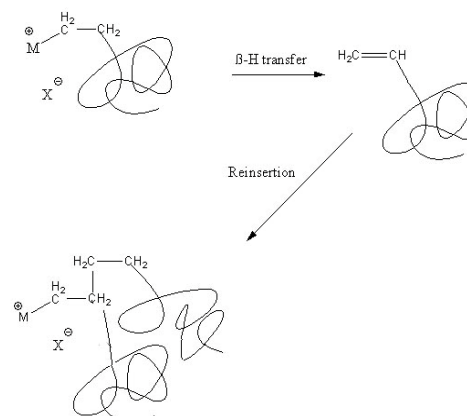

Scheme 2: A hypothetical routes for reinsertion reaction.

Figure 5: Effect of [Al]: [Fe] molar ratio on thermal behaviors of polymers obtained by catalyst A.

For catalyst B, with increasing polymerization temperature as well as [Al]:[Fe], no differences on the position of DSC melting point peaks were observed and the polymers showed sharp single melting peaks and very high crystallinity, which demonstrates that they are highly linear chains (Figure 7) [21,28].
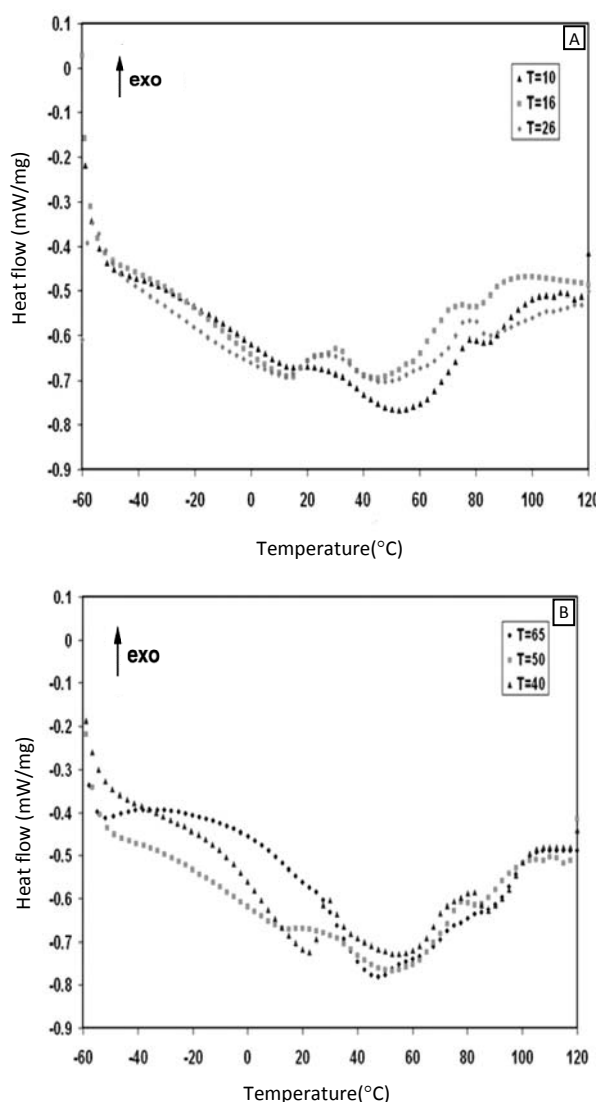
Figure 6: Effect of the polymerization temperatures on thermal behaviors of the polymers obtained using catalyst A. (A=low temperature regions, B= high temperature regions).
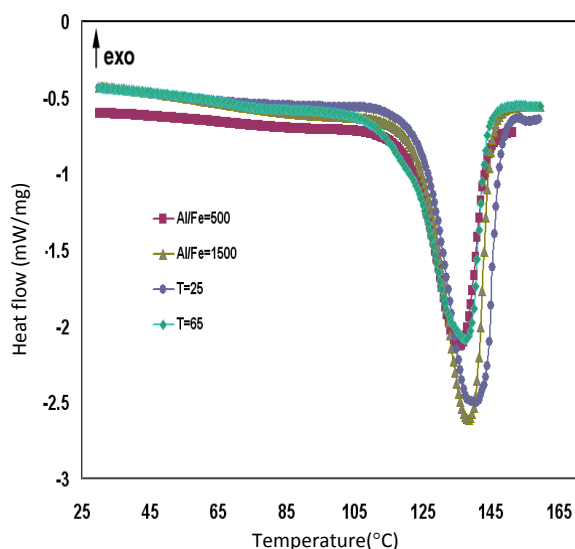
Figure 7: Effect of the polymerization temperatures and [Al]: [Fe] molar ratios on the thermal behaviors of the polymers obtained using catalyst B.

Due to the existence of less sterically hindered ligand of catalyst A, the chain transfer reactions are extremely occurred during the polymerization even at a low polymerization temperature. Although at a higher temperature it is expected to observe more and broad peaks because of the high rate of transfer reactions, it is conceivable that this trend is inversed by another phenomenon called reinsertion. As illustrated in Scheme 2, the reinsertion reaction needs higher activation energy than the other transfer reactions, and it also needs numerous short terminated chains, which are still susceptible to coordinating with the metal center around the catalyst. Both of these requirements can be provided by increasing the temperature. Therefore, we believe that at a higher temperature, due to the frequent re-insertion reaction of "monomer-like chains" (short terminated chains as in our recent report [29]), the observed peaks are broadened. The possible overlap of the broadened peaks may lead to a decrease in the number of the peaks.

High temperature ^{13}C NMR spectroscopy was also performed for some obtained polymers by catalyst A (Figure 8). The ^{13}C NMR analysis of the polymers arising from catalyst A based on Galland et al. calculation method [30] revealed highly linear

structures of the polymer (Figure 8). Indeed, the signals detected at 13.5, 22.3, and 31 ppm are only due to chain ends. Their relatively high intensity is due to low molar masses [20,21,30,31].

For late transition metal ethylene oligomerization catalysts, chain transfer generally implies with β–hydrogen transfer process leading to the formation of α-olefins. This process is dominant even in the presence of relatively high concentration of alkyl aluminum as the cocatalyst [19]. Besides the presence of linear α-olefins as a result of β-hydride transfer reactions, it is reasonable to assume the presence of alkanes as a result of chain transfer to aluminum compound (MAO) as was reported elsewhere [18,21]. The number average molecular weights (Mn) of the α-olefinic part of the polymer chain have been calculated by ^{13}C NMR according to the method of Galland et al. (Table 1). As can be seen, the highest number molecular weight obtained at the lowest polymerization temperature and lowest [Al]:[Fe] molar ratio. The behavior could be due to the higher number of vinyl chain ends, which is increased by lower possibilities of the occurrence of chain transfer reactions, especially β–hydride transfer reaction as already reported [9-11,19,29].
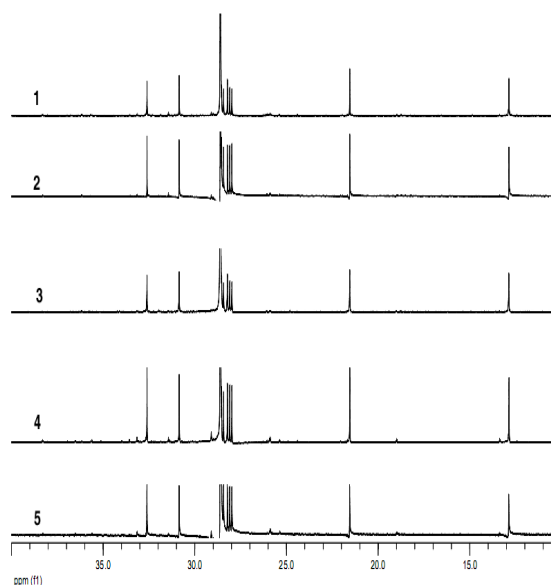

Figure 8: ^{13}CNMR spectrum of some oligomers obtained with catalyst A.

Table 1: The (Mn) of α- olefinic part of the polymer chain obtained by catalyst A using ^{13}C NMR; polymerization conditions: toluene=80 ml, polymerization time = 30 min, [Fe] = 0.006 mmol, and stirrer speed = 800 rpm.

Sample	[Al]:[Fe]	Polymerization Temperature (°C)	Mn (α -olefin)
1	1500	5	361
2	1500	25	260
3	1500	65	253
4	500	25	349
5	2500	25	264

CONCLUSIONS

It was demonstrated that the size of the substituent is the factor that controls the ability of catalyst to produce polymers instead of oligomers. Catalyst A was more active toward ethylene polymerization than catalyst B. Catalyst A produced oligomers showing a multimodal thermal behavior; however, catalyst B produced high linear polyethylene products. Polymerization temperatures affected the thermal property of catalyst A in terms of shape and numbers of melting points of the obtained polymers; however, [Al]:[Fe] molar ratio did not influence the thermal behavior of the obtained polymer. It was also showed that catalyst A produced linear oligomers, containing α-olefinic part with the number average molecular weight in range of 260 -361 gr/grmol.

REFERENCES

[1] Hoff R. and Mathers R. T., *Handbook of Transition Metal Polymerization Catalyst*, New Jersey: A John Wiley & Sons, Inc., Publication, **2010**.

[2] Kaminsky W., *Metal-organic Catalysts for Synthesis and Polymerization*, Springer: Verlag, Heidelberg, **1999**.

[3] Montagna A. A., Burkhart R. M., and Dekmezian A. H., "The Evolution of Single-Site Catalysis," *Chemical Technology*, **1997**, *27*, 26-31.

[4] Johnson L. K., Killian C. M., and Brookhart M., "New Pd (I1)- and Ni (I1)-based Catalysts for Polymerization of Ethylene and α-Olefins," *Journal of American Chemical Society*, **1995**, *117*, 6414-6415.

[5] Ittel S. D., Johnson L. K., and Brookhart M., "Late-metal Catalysts for Ethylene Homo and Copolymerization," *Chemical Reviews*, **2000**, *100*, 1169-1203.

[6] Mecking S., "Olefin Polymerization by Late Transition Metal Complexes: a Root of Ziegler Catalysts Gains New Ground," *Angewandte Chemie International Edition*, **2001**, *40*, 534-540.

[7] Small B. L. and Brookhart M., "Bennett AMA, Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene," *Journal of American Chemical Society*, **1998**, *120*, 4049-4050.

[8] Bennett A. M. A., "Iron Catalyst for the Polymerization of Olefins," U. S. Patent, 6214761, April **10 2001**.

[9] Britovsek G. J. P., Gibson V. C., Kimberley B. S., Maddox P. J., et al. "Novel Olefin Polymerization Catalysts Based on Iron and Cobalt," *Chemical Communications*, **1998**, *7*, 849-850.

[10] Small B. L. and Brookhart M., "Iron-based Catalysts with Exceptionally High Activities and Selectivities for Oligomerization of Ethylene to Linear Olefins," *Journal of American Chemical Society*, **1998,** *120*, 7143-7144.

[11] Britovsek G. J. P., Gibson V. C., and Wass D. F., "The Search for New Generation Olefin Polymerization Catalysts: Life Beyond Metallocenes," *Angewandte Chem. International Edition,* **1999**, *38*, 428-447.

[12] Bennett A. M. A., "Polymerization of Ethylene with Specific Iron or Cobalt Complexes, Novel Pyridine bis (Imines) and Now With Iron and Cobalt," **1998**, WO9827124.

[13] McTavish S., Britovsek G. J. P., Smit T. M., Gibson V. C., et al., "Iron-based Ethylene Polymerization Catalysts Supported by Bis(Imino)Pyridine Ligands: Derivatization Via Deprotonation/ Alkylation at the Ketimine Methyl Position," *Journal of Molecular Catalysis A: Chemical,* **2007**, *261*, 293-300.

[14] Ionkin A. S., Marshall W. J., Adelman D. J., Shoe A. L., et al., "Nitro-substituted Iron(II) Tridentate Bis(imino)pyridine Complexes as High-temperature Catalysts for the Production of α-olefins," *Journal of Polymer Science: A Polymer Chemistry*, **2006**, *44*, 2615-2635.

[15] Zohuri G. H., Damavandi S., Dianat E., Sandaroos R., et al., "Novel Functionalized Bis(Imino)Pyridine Cobalt(II) Catalysts for Ethylene Polymerization," *International Journal of Polymer Material,* **2011**, *60*, 776-786.

[16] Damavandi S., Zohuri G. H., Sandaroos R., and Ahmadjo S., "Novel Functionalized Bis(imino)pyridine Cobalt(II) Catalysts for Ethylene Polymerization," *International Journal of Polymer research,* **2012**, *19*, 9796-9800.

[17] Zohuri G. H., Seyedi S. M., Sandroos R., Damavandi S., et al., "Novel Late Transition Metal Catalysts Based on Iron: Synthesis, Structures and Ethylene Polymerization," *Catalysis Letter*, **2010**, 140, 160-166.

[18] Britovsek G. J. P., Bruce M., Gibson V. C., Kimberley B. S., et al., "Iron and Cobalt Ethylene Polymerization Catalysts Bearing 2,6- Bis(Imino)Pyridyl Ligands: Synthesis, Structures and Polymerization Studies," *Journal of American Chemical Society*, **1999**, *121*, 8728-8740.

[19] Britovsek G. J. P., Mastroianni S., Solan G. A., Baugh S. P. D., et al., "Oligomerization of Ethylene by Bis(Imino)Pyridyl Iron and Cobalt Complexes," *Chemical European Journal*, **2000**, 6, 2221-2231.

[20] Britovsek G. J. P., Baugh S. P. D., Hoarau O., Gibson V. C., et al., "The Role of Bulky Substituents in the Polymerization of Ethylene Using Late Transition Metal Catalysts: A Comparative Study of Nickel and Iron Catalysts," *Inorganica Chimica. Acta*, **2003**, *345*, 279-291.

[21] Gibson V. C. and Solan G. A., "Iron-Based and Cobalt-Basad Olefin Polymerization Catalysts" *Top Organomet Chem*, Berlin Heidelberg, Springer-Verlag, **2008**.

[22] Rieger B. L., Saunders B. L., Kacker S., and Striegler S., "Late Transition Metal Polymerization Catalysis," **2003**, Wiley-VCH:Weinheim.

[23] Ahmadjo S., Arabi H., Nekoomanesh M., Zohuri G. H., et al., "Comparative Study of Copolymerization and Terpolymerization of Ethylene/ Propylene/ Diene Monomers Using Metallocene Catalyst," Macromol React. Eng., 2010, 4, 707-714.

[24] Mortazavi M. M., Arabi H., Zohuri G. H., Ahmadjo S., et al., "Copolymerization of Ethylene/α-olefins Using Bis (2-Phenylindenyl) Zirconium Dichloride Metallocene Catalyst: Structural Study of Comonomer Distribution," *Polymer International*, **2010**, *59*, 1258-1265.

[25] Justino J., Dias A. R., Ascenso J., Marques M. M., et al., "Polymerization of Ethylene Using Metallocene and Aluminoxane Systems," *Polymer International*, **1997**, *44*, 407-412.

[26] Fink G., Steinmetz B., Zechlin J., Przybyla C., et al., "Propene Polymerization with Silica-Supported Metallocene/MAO Catalysts," *Chemical Reviews*, **2000**, *100*, 1377-1390.

[27] Busico V., Talarico G., and Cipullo R., "Living Ziegler-Natta Polymerizations: True or False," *Macromolecular Symposia*, **2005**, *226*, 1-16.

[28] Chen J., Huang Y., Li Z., Zhang Z., et al., "Syntheses of Iron, Cobalt, Chromium, Copper and Zinc Complexes With Bulky Bis(Imino)Pyridyl Ligands and their Catalytic Behaviors in Ethylene Polymerization and Vinyl Polymerization of Norbornene," *Journal of Molecular Catalysis A: Chemical*, **2006**, *259*, 133-141.

[29] Damavandi S., Samadieh N., Ahmadjo S., Etemadinia Z., et al., "Novel Ni-based FI Catalyst for Ethylene Polymerization," *European Polymer Journal*, **2015**, *64*, 118-125.

[30] Galland G. B., Quijada R., Rojas R., Bazan G., et al., "NMR Study of Branched Polyethylenes Obtained with Combined Fe and Zr Catalysts," *Macromol*, **2002**, *3*, 339-345.

[31] Pelascini F., Peruch F., Lutz P. J., Wesolek M., et al., "Pyridine Bis (Imino) Iron and Cobalt Complexes for Ethylene Polymerization: Influence of the Aryl Imino Substituents," *European Polymer Journal,* **2005**, *41*, 1288-1295.