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ORIGINAL PAPER

Homo- and co-polymerization of polar and non-polar olefinic monomers using bicenter cobalt-diimine catalysts

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ABSTRACT

Bicenter (BCn) cobalt-bis(imine) catalysts were synthesized to be used for the polymerization of methyl methacrylate (MMA) and 1-hexene. The effect of catalyst structure, bridging ligand and polymerization reaction conditions was investigated. Synthesis of primary ligand (2,6-dibenzhydryl-4-ethoxyphenyl)-N=(CH$_3$)-C(CH$_3$)=O was also done. Following to that, the final ligands of the BC1 and BC2 bicenter catalysts were prepared via reacting the primary ligand with 2,3,5,6-tetramethylbenzene-1,4-diamine and 4,4-methylenedianiline bridges, respectively. The BC1 catalyst demonstrated higher activity than the BC2 catalyst. The highest activity for the BC1 catalyst was obtained when the co-catalyst to catalyst molar ratio was [Al]/[Co]=1500:1, and the polymerization temperature was 40°C. In comparison, the BC2 catalyst demonstrated the highest activity and higher thermal stability in the conditions of: [Al]/[Co]=500:1 ratio and 70°C polymerization temperature. The ^{1}H NMR analysis results revealed that the highest branching density for the poly(methyl methacrylate) (PMMA) produced by the BC1 and BC2 catalysts was 222 and 249 branches per 1000 carbon atoms, respectively. The PMMA synthesized with the BC2 catalysts had the highest syndiotacticity (59%). The polymer produced with the bicenter catalyst (BC1) showed a relatively broad molecular weight distribution (2.9), according to the GPC analysis results. The synthesized catalysts demonstrated appropriate activity for the polymerization of MMA, but only moderate activity for 1-hexene monomer. **Polyolefins J (2024) 11: 125-136**

Keywords: Catalytic polymerization; cobalt catalyst; bicenter catalyst; α-diimine; poly(methyl methacrylate).

INTRODUCTION

At the same time as the polyolefin production industry has grown, the global thermoplastics consumption market has developed significantly [1,2]. The rapid growth of catalytic systems is one of the reasons for increased production and consumption of these types of polymers, although recycling is also a major problem. With Ziegler's important discovery in 1959, this coordination polymerization system, later known as the Ziegler-Natta catalytic system, demonstrated its unique capabilities in the olefin polymerization, despite of the fact that the copolymerization and polymerization capability of polar monomers was relatively low [3,4]. Metallocene catalytic systems with special properties such as increased activity and higher co-monomer insertion were introduced [5,6]. With the discover of late transition metal catalysts it was revealed that these catalysts are very suitable for polymerization and copolymerization of polar monomers due to lower exophilicity compared to the previous catalytic systems. The polymers formed with using the late transition

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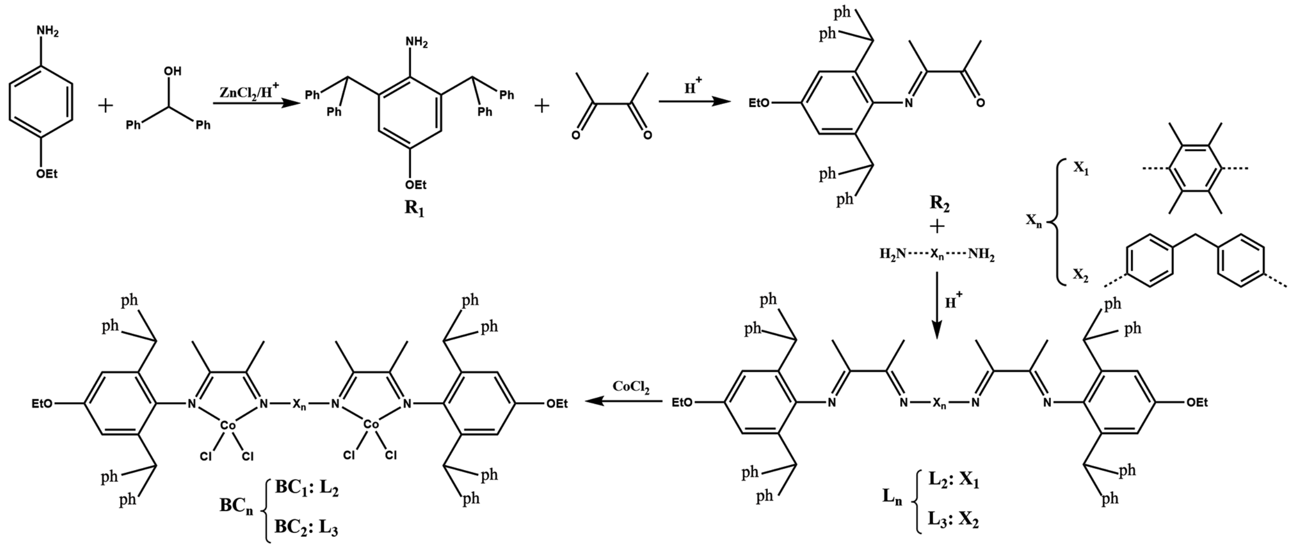
metal catalysts have a wide range of properties. These properties are directly dependent on the catalyst structure (metal and ligand type), the number of metal centers, and the polymerization reaction conditions [7-11]. Brookhart group reported the first samples of olefin polymerization with the late transition metal catalysts. They demonstrated that bulky *α*-diimine ligands in catalysts based on Ni and Pd can produce high molecular weight polyolefins [12]. The requirement for thermal stability of the later transition metal catalysts at high polymerization temperatures (60°C), which is typical for industrial applications, prompted researchers to design the structure of these types of catalysts. Zohuri's team synthesized monocenter and bicenter catalysts based on nickel and palladium and used them to polymerize ethylene. The nickel catalyst was active even at temperatures above 90°C, whereas the palladium catalyst was only active at temperatures below 80°C [13,14]. Multi-center catalysts cause diversity and expansion in the properties of produced polymers due to the synergistic effect of metal centers with different structures and connections in comparison to the diverse structures of monocenter catalysts. According to the results of the comparison with their corresponding mononuclear catalyst, the existence of cooperativity between the bicenter catalyst main reports focused on properties such as changes in catalytic activity, microstructure, molecular weight and molecular weight distribution, selectivity, tacticity, and the amount of cooperativity in the chain. Khoshsefat *et al*., [15,9] conducted extensive research on monocenter and bicenter diimine catalysts based on nickel metal for ethylene polymerization. Due to the effect of bicenter as well as electronic and spatial effects on the main structure, monocenter catalysts typically showed less activity and bicenter catalysts worked more successfully [15]. Dechal *et al.,* reported monocenter and bicenter nickel catalysts for the polymerization of 1-hexene, as well as using different ethylaluminum sesquichlorid (EASC) which used as cocatalyst. It specifically produced the highest viscosity average molecular weight polyhexene using mononuclear catalyst [16]. Diiminopyridine complexes can be excellent polymerization catalysts for ethylene and higher olefins such as 1-pentene, 1-hexene, and 1-octene, and they can also oligomerize these monomers, while ligand substitutions used for the catalyst have a strong effect on the performance of such catalysts [17]. Diimine catalysts have favorable properties and can be used as catalysts for polar acrylic monomers that reported by Avar *et al.,* [18]. They investigated copolymerization of 1-hexene with butyl acrylate and tert-butyl acrylate monomers at ambient temperature using a nickel diimine catalyst. Kim *et al.,* investigated iron (Π), nickel (Π), and cobalt (Π) catalysts for the polymerization of MMA in the presence of MMAO with designing substitutions in the main skeleton of the ligands [19]. Compared to metallocene catalysts, all synthesized LTM catalysts showed moderate activity. Nickel-based catalysts had the highest activity among the used LTM catalysts, while iron catalysts had the lowest activity, and catalytic activity increased with increasing polymerization temperature [19]. Abedini *et al.,* reported copolymerization of ethylene and MMA with camphyl ligand using a nickel catalyst; poly(methyl methacrylate) with a glass transition temperature of about 130°C was obtained using MMAO cocatalyst [20]. The copolymerization of 1-hexene and MMA with different nickel diimine catalysts was reported by Zohuri group (2021); the catalyst showed high activity (6.9×10^4 g P/ mol Ni.h), and the microstructure of the resulting PMMA was mostly atactic [21]. Wang *et al.,* used Pd-based β-ketoimino catalyst for MMA polymerization; the resulting PMMA had moderate syndiotactic microstructures [22]. Zheng *et al.,* investigated the electronic effects of nickel and palladium amine-imine catalysts in the copolymerization of ethylene with methacrylate; the electron-donating group in ligand resulted in better copolymerization of the monomers with platinum catalyst [23].

So far, for the polymerization and oligomerization of α-olefins, a large number of transition metal complexes with nickel- and palladium-based α-diimine ligands have been synthesized and studied. However, there have been fewer reports on bicenter cobalt complexes containing α-diimine and their use in MMA polymerization [19-22]. In this research work, to investigate the use of bicenter catalysts for the polymerization of olefins, MMA was selected, and in this regard, the performance of bicenter catalysts in different polymerization conditions and the effect of the catalyst structure on the microstructure of the produced polymer were studied.

EXPERIMENTAL

Materials

1,4-Diamine, 4,4-methylenedianiline, 4,2-trimethylaniline, formic acid, para-ethoxyaniline, diphenylmethanol



Scheme 1. Synthetic route of ligands and catalysts.

(benzhydryl), 3,5,6-tetramethylbenzene, para-toluene sulfonic acid, and cobalt chloride were provided by Merck Chemical Co. All solvents, including methane dichloride and diethyl ether, were distilled before use [16]. Toluene (Merck, >99 %) was refluxed over calcium hydride for 24 h and then refluxed over sodium and benzophenone, distilled, and stored over molecular sieves under dry nitrogen. The monomers,1-hexene and methyl methacrylate were also distilled and kept over activated molecular sieve 4A/13X.

Polymerization

The polymerization of MMA and 1-hexene (liquid monomers) was carried out in a 100 mL round bottom flask reactor and the contents of the mixture were mixed using a magnetic stirrer. Dried toluene (6 mL) was added to the glass reactor for the polymerization of MMA and 1-hexene at room temperature under nitrogen gas. Then the stirring reactor was filled with monomer (10-20 mL) and after a few minutes, the desired amount of MMAO cocatalyst was added. Finally, the catalyst (4 µmol) dissolved in toluene (2-4 mL) was added to the glass reactor, and the polymerization process began at desired polymerization temperature (25-60°C). The reaction was stopped after the desired time (2-24 hour), and the obtained solution was added to a solution containing acidic methanol (10%) to precipitate the polymer. The polymer was then dried and weighed.

Characterization

Infrared spectroscopy (FTIR, device model AVATAR 370A) was used to identify functional groups in the synthesis of ligands and catalysts, as well as to identify the polymers. Gel permeation chromatography (GPC, Agilent-1100) in dry tetrahydrofuran at room temperature was used to determine the molecular weight of the polymers. Proton nuclear magnetic resonance (^{1}H NMR, Bruker AC 300 model device) was used to identify the synthesized ligands, as well as the polymers and copolymers obtained, and it was used to calculate the spatial order of the polymers chain. The samples were dissolved in deuterated chloroform solvent.

Preparation of ligands and catalysts

Synthesis of R1 and R2 ligands

Synthesis of ligands was carried out in accordance with our previous articles [13,14]. The preparation method is summarized in Scheme 1, and ^{1}H NMR and FTIR methods were used to confirm the structures (see Figures S1-S4 in Supporting Information (SI)). In a 100 mL flask, para-ethoxyaniline and diphenylmethanol (benzhydryl) were mixed in a molar ratio of 1:2 in the presence of zinc dichloride in an acidic medium to synthesize amine with bulky substitutions (R1). Following to that, in the presence of a small amount of formic acid, as a catalyst, diacetyl (3.5 mmol, 0.3 mL) was mixed with methanol and the synthesized amine 2,6-dibenzhydryl 4-ethoxyphenyl (R1) (3.1 mmol) was added drop wise. The solution was stirred for four days at ambient temperature. TLC technique was used to monitor the reaction progress. The yellow precipitate was filtered and dried, and the resulting ligand was designated as R2 (Scheme 1).

Synthesis of L2 ligand

A solution of R2 ligand (1.2 mmol, 1 g) was added in a round-bottom flask with 50 mL of toluene. The compound 2,3,5,6-tetramethylbenzene-1,4-diimine (0.9 mmol, 0.5g) was added to the reaction vessel in the presence of a small amount of para-toluene sulfonic acid, as a catalyst. The reaction was refluxed and stirred for 7 days. The Dean-Stark system was installed to remove the water produced during the reaction, and the progress of the reaction was monitored using TLC technique. The solvent was removed using vacuum, and a precipitate was formed with adding diethyl ether (Scheme 1). The resulting precipitate was separated and washed several times with diethyl ether, yielding the ligand which named L2 (the product was characterized using FTIR technique, see Figure S5 in SI)

Synthesis of L3 ligand

The molar ratio of R2 ligand to the bridge compound (4,4-methylenedianiline) was two to one in the synthesis of L3 ligand, and slightly more than R2 ligand was used to ensure completion of the reaction. To the flask of ligand R2 (1.2 mmol), first toluene (about 50 mL) was slowly added in the presence of para-toluenesulfonic acid, as a catalyst, and then 4,4-methylenedianiline (2.2 mmol). The Dean-Stark system was then installed to reflux for seven days. The obtained brown precipitate was filtered and washed with diethyl ether at the end of the reaction. Scheme 1 depicts the L3 ligand synthesis method (for FTIR spectra see Figure S6 in SI).

Synthesis of bicenter cobalt catalysts BC1 and BC2

A solution of synthesized L2 ligand (0.1 g) in dichloromethane (15 mL) was added dropwise to a solution of cobalt (Π) chloride (0.02 g) and dry dichloromethane (20 mL) in an atmosphere of argon gas. A light brown solution was prepared. After 5 days of stirring at room temperature, the color of the solution changed to green. The obtained green precipitate was filtered, washed several times with diethyl ether, and dried. The BC1 catalyst synthesis method is depicted in Scheme 1. The synthesis of BC2 catalyst is similar to that of the BC1, with the exception that L3 ligand was used instead of the L2 ligand. After 7 days, a dark brown precipitate was obtained, indicating the presence of BC2 catalyst (for FTIR spectra see Figure S7 and S8 in SI) (Scheme 1).

Table 1. Polymerization of MMA using BC1 and BC2 catalysts.

Sample code	[Al]/[Co]	Polymer weight (g)	Activity (g PMMA/mmol cat. h)
BC_1S_1	500	0.7	10.9
BC_1S_2	1000	0.8	12.9
BC_1S_3	1500	1.2	17.9
BC_1S_4	2000	0.6	8.6
BC_2S_1	250	0.1	1.5
BC_2S_2	500	0.5	8.4
BC_2S_3	1000	0.4	6.4
BC_2S_4	1500	0.3	4.2
BC_2S_5	2000	0.3	4.2

Polymerization conditions: catalyst= 2μmol, MMA monomer=10 mL, reaction temperature= 27°C, reaction time= 24 h, toluene=10 mL

RESULTS AND DISCUSSION

Bicenter cobalt (Π) catalytic systems with MMAO co-catalyst were used for the polymerization of polar and non-polar monomers, and the effects of different polymerization factors, such as polymerization time, polymerization temperature, and the ratio of co-catalyst to catalysts, were investigated. Finally, the microstructures of the resulting polymers were identified using various methods.

Polymerization of methyl methacrylate

Effect of co-catalyst concentration

Previously monocenter analogue of catalyst was used for methyl methacrylate polymerization [14]. The highest polymerization activity (8.6 g PMMA/ mmol cat. h) was obtained at [Al]/[Co]=1000:1 molar ratio and at room temperature [14]. Adjacent of metal centers in the bicenter catalysts provided by the ligand structures could increase or decrease activity in comparison with monocenter ones, due to their steric hindrance or electronic effects on polymerization [13-16]. The optimum molar ratios ([Al]/[M]=1500) obtained for dinuclear Ni-based catalyst were reported by Zohuri's team in the polar monomer copolymerization, with dinuclear nickel catalyst higher vinyl monomers incorporation and suitable activity of catalysts [21].

The obtained results (Table 1) revealed that increasing the [Al]/[Co] molar ratio up to 1500:1 increased the activity of the BC1 catalyst, however, the higher molar ratio up to 2000, sharply decreased the catalyst activity. In addition to alkylating and activating the active center of the catalyst, the role of MMAO in the polymerization environment is to remove impurities and pollution that require a sufficient amount of cocatalyst. The co-catalyst prevents the entry of the monomer into the activated centers at a higher molar ratio, thus reducing the activity [19,20].

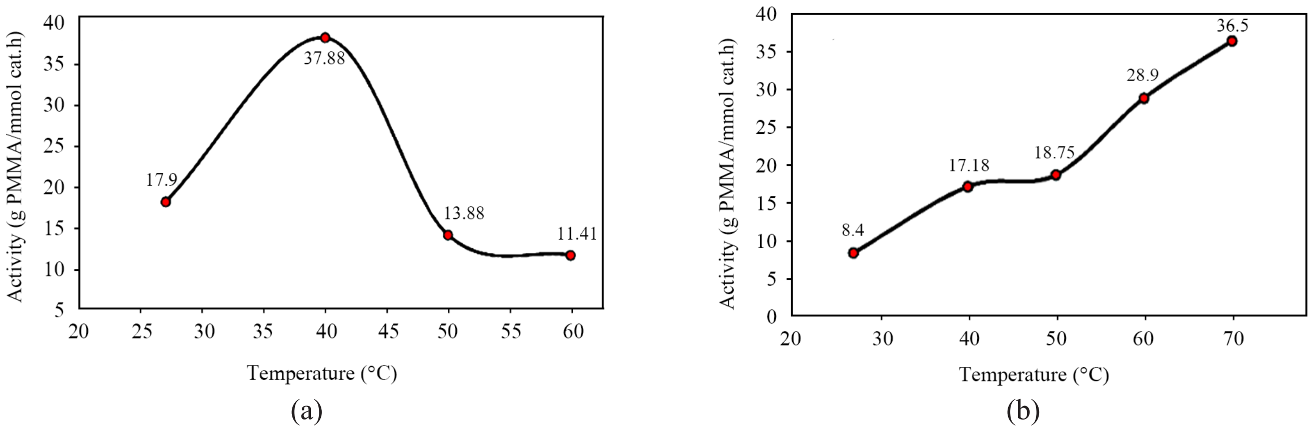
The general structure of the catalyst, as well as the bridge connecting two metal active centers are two very important and influential factors in the catalyst behavior. The second metal active center has the ability to alter the behavior of the catalyst. In fact, the nature (rigid or flexible) and length of the bridge between two active centers control these electronic tendencies, which affect the activity of the catalyst, the stability of the catalyst, and the properties of the obtained polymer [15,21]. The nature of the bridge structure in catalysts can affect the amount of polymerization activity. The activity of BC2 catalyst was lower than that of the BC1 catalyst, and replacing the flexible bridge (4,4-methylenedianiline) with the rigid bridge (2,3,5,6-tetramethylaniline) resulted in more spatial crowding in the BC2 catalyst. As a result, monomer penetration into the active centers of the catalyst has become more difficult, and so the catalyst activity has decreased. At 27°C, MMA polymerization with the BC2 catalyst was also investigated (Table 1). The activity of the catalyst increased with a relatively sharp slope when the molar ratio of the co-catalyst to the catalyst was increased from [Al]/[Co]=250 to [Al]/[Co]=500. This is due to the increase in alkylation of the active centers. However, the activity was almost fixed between 1000 and 2000 molar ratio. One of the advantages of this catalyst is that the optimal molar ratio of the co-catalyst to the catalyst is lower than that of the BC1. The synergistic effect of activity in bicenter catalysts, on the other hand, is determined by the nature and length of the bridge between the two centers. The behavior of the bicenter catalysts can be improved or modified by changing the bridge structure, which can be rigid, flexible, or rigid/flexible [13-16].

Effect of polymerization temperature

To investigate the effect of temperature on the polymerization behavior of BC1 catalysts, polymerization with a specific amount of catalyst (2×10^{-6} mol) in a constant molar ratio ([Al]/[Co]=1:1500), polymerization time (24 h) was investigated at different temperatures (27, 40, 50, and 60°C). The best polymerization temperature for obtaining the highest product using the BC1 catalyst was 40°C (Figure 1, part (a)). The rate-determining step before reaching the optimal temperature includes the transfer and absorption of monomer to the active centers, which increases the probability of the monomer entering to the active centers as well as the activation energy required for the polymerization. As a result, in the early stages, increasing the temperature facilitates and accelerates the formation of active centers, increasing the rate of alkylation, speeding up the reaction, and ultimately causing more polymer production. However, exceeding the optimum temperature causes the destruction of active catalytic centers and a decrease in the solubility of the monomer in the reaction medium, resulting in a decrease in the catalyst activity [20]. Investigating the effect of temperature on the polymerization behavior of the BC2 catalyst, on the other hand, revealed a different behavior than the previous catalyst. Temperatures ranging from 27 to 70°C were used for the polymerization (Figure 1, part (b)). The trend of activity changes was upward as the polymerization temperature increased. As a result, the prepared BC2 catalyst was more thermally stable than the BC1 catalyst.

Kinetic study

To investigate the effect of polymerization time on the catalyst behavior, MMA was polymerized in the



(a) (b)

Figure 1. Effect of polymerization temperatures on the activity of (a) BC1 and (b) BC2 catalysts. Polymerization conditions: catalyst=2μmol, MMA monomer=10 mL, reaction time= 24 h, toluene=10 mL.

presence of 2×10^{-6} mol catalyst under the optimal conditions of: [Al]/[Co]=1500:1, temperature of 40°C and for different times of 2, 6, 12, and 24 hours (Table 2). The polymerization activity increased up to 2 h polymerization time, however, the catalyst activity then decreased to some extent as the reaction time was increased further. The reason for these decreases could be duo to the presence of the polymer chain connected to the active center of the catalyst makes penetration of the monomer more difficult [21]. In this reduction, irreversible destruction of active centers and poisoning of the catalyst with polar monomers may take place. The effect of polymerization time, on the other hand, was investigated for the catalyst BC2 at a temperature of 70°C and a ratio of [Al]/[Co]=500:1 (Table 2). It was discovered that as polymerization time increased, the activity of this catalyst reached the maximum value and then decreased. Due to the presence of the polymer chain connected to the catalytic active center, the possibility of monomer penetration becomes more difficult with the passage of time and the activity of the catalyst decreases for a long time [22].

Polymerization of 1-hexene

In general, the synthesized catalysts demonstrated little activity for the polymerization of 1-hexene at low monomer concentrations. The effect of [Al]/[Co] ratio on the activity of BC1 and BC2 catalysts for 1-hexene polymerization was investigated. The obtained results (Table 3) demonstrated that increasing the molar ratio of [Al]/[Co] to the optimal ratio increases the activity of the BC1 catalyst due to increased alkylation of the catalyst's active centers. Furthermore, at higher molar ratios, the addition of the co-catalyst prevented 1-hexene monomer coordination to the active centers of the catalyst [24,25] and reduced the activity, however, when compared to the BC1 catalyst, the BC2 catalyst showed significantly less activity in the polymerization of 1-hexene, and practically no product was obtained at very low [Al]/[Co] ratios, which is likely due to the structure of the catalyst and the type of bridge used in the structure of the catalyst [15,21].

Table 2. MMA polymerizations with BC1 and BC2 catalysts at different polymerization times.

Sample code	Time (h)	Polymer weight (g)	Activity (g PMMA/ mmol cat. h)
BC_1t_1 [(a)]	2	0.4	66.7
BC_1t_2 [(a)]	6	0.9	61.1
BC_1t_3 [(a)]	12	1.5	46.9
BC_1t_4 [(a)]	24	2.4	37.0
BC_2t_1 [(b)]	2	0.2	33.7
BC_2t_2 [(b)]	6	0.6	34.5
BC_2t_3 [(b)]	12	1.3	39.4
BC_2t_4 [(b)]	24	2.3	36.5

Polymerization reaction conditions: (a) catalyst=2μmol, MMA monomer=10 mL, [Al]/[Co]=1500:1, reaction temperature= 40°C, toluene solvent= 10 mL. (b) catalyst= 2 μmol, MMA monomer=10 mL, molar ratio= [Al]/[Co]=500:1, reaction temperature= 70°C, toluene=10 mL

Copolymerization of 1-hexene with MMA with BC1 catalyst

Because the BC2 catalyst did not show good activity in the polymerization of 1-hexene, only the BC1 catalyst was used in the copolymerization of 1-hexene and MMA. Different concentrations of MMA monomer were added to the polymerization reactor in the presence of a fixed concentration of 1-hexene monomer to investigate the effect of MMA concentration on activity of the BC1 bicenter catalyst. The results showed that by increasing the MMA monomer, the activity of the catalytic system increased (Figure 2). The presence of polar monomer increased the activity of the catalyst in copolymerization for the following reasons: the effect of the methyl group in the beta MMA carbon, which largely prevents the coordination of the carbonyl group to the active center of the catalyst and the formation of a six-membered chelate [26], or due to the high acid strength of MMAO, it protects the carbonyl oxygen group in the MMA monomer and prevents the catalyst from being poisoned in the presence of this monomer [27].

Characterization

FTIR spectroscopic analysis was used to investigate the microstructure of the obtained polymer samples. Comparing the FTIR spectra of PMMA obtained from the two synthesized catalysts (Figure 3) reveals that the polymers obtained from the two bicenter catalysts

Table 3. The results of 1-hexene polymerizations with BC1 and BC2 catalysts.

Sample code	[Al]/[Co]	Polymer weight (mg)	Activity (g PH/ mmol cat. h)
BC_1H_1	500	2	0.03
BC_1H_2	1000	7	0.11
BC_1H_3	1500	80	1.2
BC_1H_4	2000	40	0.6
BC_2H_1	500	0	0
BC_2H_1	1000	0	0
BC_2H_1	1500	0	0
BC_2H_1	2000	10	0.2

Polymerization reaction conditions: catalyst=2μmol, 1-hexene=10 mL, polymerization temperature=25°C, reaction time=24 h, toluene=10 mL

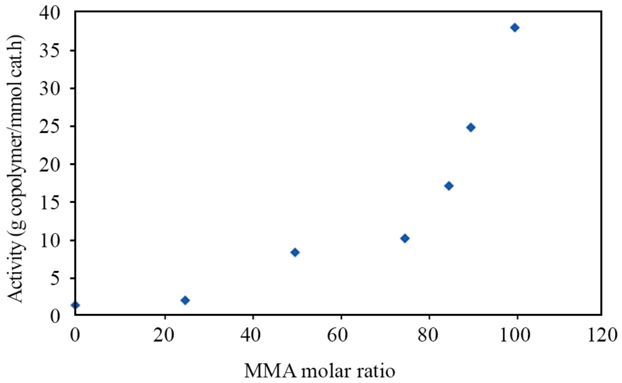


Figure 2. Effect of MMA concentration on the activity of copolymerization. Polymerization conditions: catalyst=2μmol, [Al]/[Co]=1500:1, reaction temperature=40°C, reaction time= 24 h and toluene=10 mL.

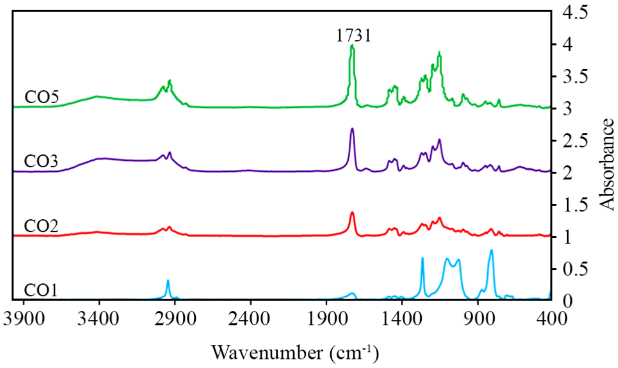


Figure 4. Comparison of FTIR spectra of the copolymers synthesized with the BC1 catalyst with different ratios of MMA in feed CO1(25), CO2(50), CO3(75), CO4(90). For polymerization conditions see Table 6.

have same structures, implying that these two catalysts most likely use the same polymerization mechanism, though NMR analysis was used to investigate the microstructure more precisely.

The FTIR spectra of the produced copolymers CO1, CO2, CO3, CO4 containing 25, 50, 75, 90 methyl methacrylate in feed ratio are depicted in Figure 4, respectively. In all spectra, there are peaks in the 2850-3000 cm^{-1} region, which are related to the C-H stretching vibration, and there is a peak in the 1452-1486 cm^{-1} region, which is related to the CH_2 bending vibration, and a peak in the 1360-1389 cm^{-1} region, which is related to the CH_3 bending vibration, and peaks in the 1000-1200 cm^{-1} region, which are related to the stretching vibration of the C-O bond, and specially a peak in the 1731 cm^{-1} region, which is related to the carbonyl bond vibration, confirming the presence of MMA in the copolymers. The peaks at 650-1000 cm^{-1}, which are related to the bending vibration out of the C-H plane and related to the alkene (hexene) structure in the copolymer, and the weak peak in the range of 1720 cm^{-1} related to the butyl group indicate the presence of 1-hexene in the copolymer, and this peak showed more intensity in the copolymer with high content of 1-hexene (CO1 sample). The FTIR spectra of the copolymers revealed that as the MMA monomer ratio in the feed increased, so did the peak of carbonyl (1731cm^{-1}) in the copolymer, which is clearly visible in the CO5 sample (Figure 4).

Using ^1H NMR analysis, it is possible to determine the amount of spatial order, branching, and overall microstructure of the synthesized polymers, as well as the percentage of each monomer in the produced copolymers. Figure 5 depicts the ^1H NMR spectrum of one of the PMMA synthesized with the bicenter catalysts; the index peak in the 3.6 ppm region, which corresponds to the protons attached to the methoxy of methyl methacrylate group, indicates the synthesis of this polymer. Figure 6 also shows the ^1H NMR spectrum of one of the synthesized copolymers, related to the double bonds of the comonomers which eliminated. As a result, no peak in the 4.7-5 ppm range

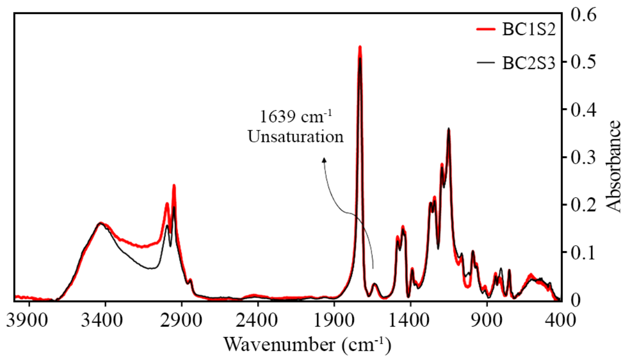


Figure 3. Comparison of FTIR spectra of poly(methyl methacrylate)obtained from BC1 and BC2 catalysts. For polymerization conditions see Table 1.

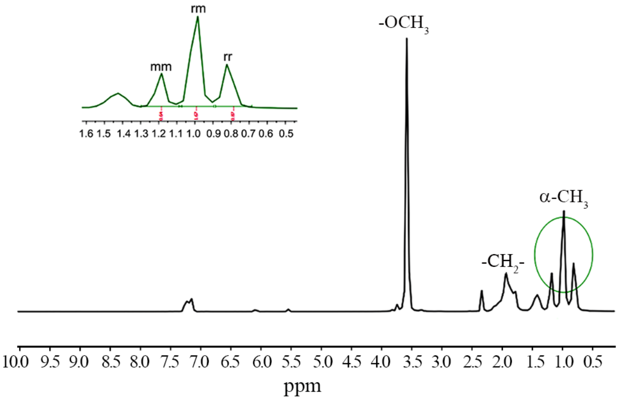


Figure 5. ^1H NMR spectrum of poly(methyl methacrylate) obtained with using the bicenter BC1catalyst. Polymerization conditions are according to Table 1.

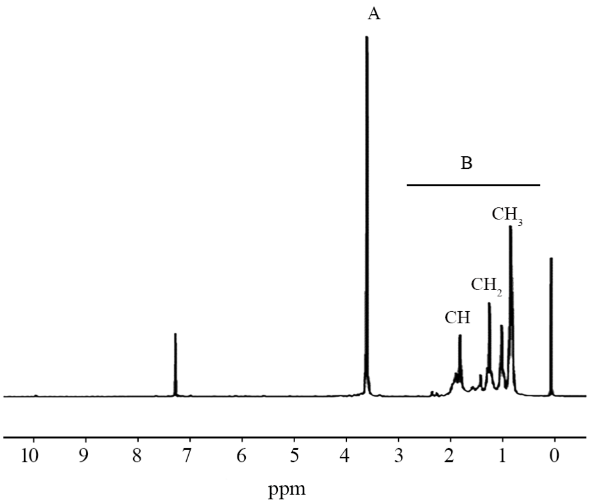


Figure 6. ^{1}H NMR spectrum of MMA copolymer obtained from the bicenter BC1 catalyst. Polymerization conditions are according to Figure 2.

was observed as expected, and on the other hand, the index peak in the 3.6 ppm region, which corresponds to protons attached to the methoxy group, can be seen in the region A of Figure 6. Also, the peaks in the 0.2-5 ppm region may be related to the aliphatic region of the two monomers (region B, Figure 6) [18,21].

Tacticity measurement

The peaks appeared in the 0.85-1.3, 1.6-1.9, and 3.6 ppm region of the PMMA ^{1}H NMR spectrum (Figures 7 and 8) correspond to -CH$_3$ protons from -C(CH$_3$)(COOCH$_3$) group, -CH$_2$-, and -OCH$_3$ proton, respectively. The percentage of syndiotactic spatial order [rr], isotactic [mm], and atactic [mr] is calculated via examining the alpha methyl (-CH$_3$) peak shown in Figures 7 and 8 and integrating from the surface area under the desired peaks [21,28].

The percentage of spatial order for the BC1 catalyst (S3 sample) is calculated as follows (Table 1 and Figure 7):

$$\%rr = \int rr \div \left(\int rr + \int mr + \int mm\right) = \frac{1}{1+0.45+0.32} = 56.5$$

(syndiotactic percentage)

$$\%mr = \int mr \div \left(\int rr + \int mr + \int mm\right) = \frac{0.45}{1+0.45+0.32} = 25.5$$

(atactic percentage)

$$\%mm = \int mm \div \left(\int rr + \int mr + \int mm\right) = \frac{0.32}{1+0.45+0.32} = 18$$

(isotactic percentage)

The percentage of spatial order for PMMA obtained by using the BC1 catalyst (BC1S3 sample, Table 1) was 56.5% syndiotactic, 18% isotactic, and 25.5% atactic, whereas that for homopolymer obtained by the BC2 catalyst (BC2S2 sample, Table 1) was syndiotactic 53.5%, isotactic 27.8, and atactic 18.7% (Figure 8). The structure of the catalyst is generally effective in the final microstructure of the resulting polymer; for example, Zohuri's team produced PMMA with bulky nickel-based diimine catalysts, which mainly showed atactic microstructure [21].

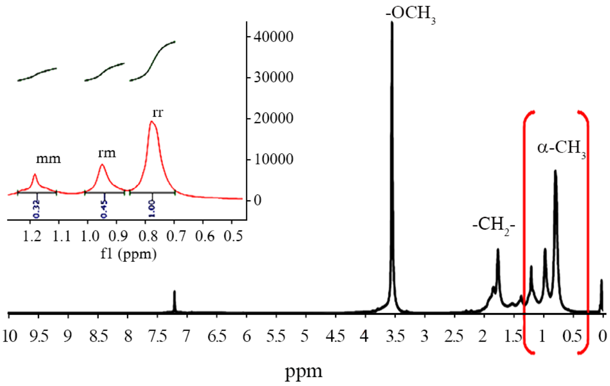


Figure 7. ^{1}H NMR of PMMA prepared using the BC1 catalyst (BC1S3 sample, Table 1).

Table 4 shows the effect of polymerization temperature on the spatial order in PMMA homopolymers obtained from the bicenter catalysts (for the ^{1}H NMR spectra of homopolymers see Figures S7-S11 in SI). Both catalysts produced polymers with a high syndiotactic percentage (above 50%), but as the polymerization temperature increased (from 27 to 60°C), the syndiotactic percentage decreased (from 55.5% to 50%). In a similar manner, Lavastre group produced syndiotactic PMMA with copper metal catalysts, and increasing the polymerization temperature (from 0 to 50°C) resulted in a decrease in

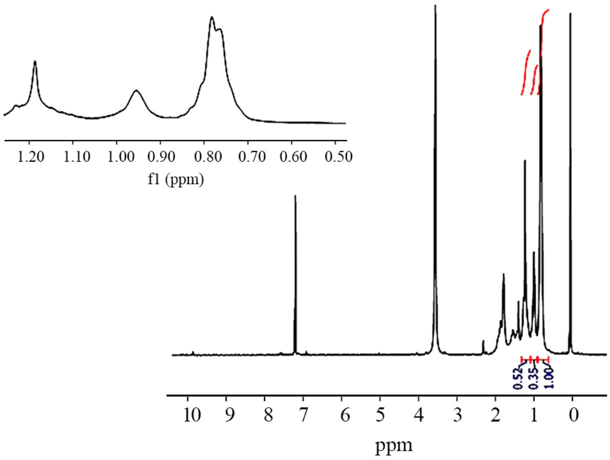


Figure 8. ^{1}H NMR of PMMA prepared using the BC2 catalyst (BC2S2 sample, Table 1).

Table 4. Results of measuring the spatial order of homopolymers synthesized at different polymerization temperatures.

Sample code	Polymerization temperature (°C)	Atactic (%)	Isotactic (%)	Syntactic (%)
BC$_1$S$_3$	27	25.5	18.0	56.5
BC$_1$T$_4$	40	36.5	8.0	55.5
BC$_1$T$_5$	50	23.0	24.0	53.5
BC$_1$T$_6$	60	28.0	22.0	50.0
BC$_2$S$_2$	27	18.7	27.8	53.5
BC$_2$T$_4$	40	30.5	17.0	52.5
BC$_2$T$_5$	50	31.0	10.0	59.0
BC$_2$T$_6$	60	30.2	18.5	51.3
BC$_2$T$_7$	70	31.0	11.0	58.0

Polymerization conditions are according to Table 1 and Figure 1.

Table 5. Results of branching of synthesized polymers using MMAO co-catalyst.

Sample code	Polymerization temperature (^{0}C)	Branching density (CH$_3$/1000 C)
BC$_1$S$_3$	27	222
BC$_1$T$_4$	40	209
BC$_1$T$_5$	50	201
BC$_1$T$_6$	60	210
BC$_2$S$_2$	27	249
BC$_2$T$_4$	40	201
BC$_2$T$_5$	50	216
BC$_2$T$_6$	60	211
BC$_2$T$_7$	70	236

Polymerization conditions are according to Table 1 and Figure 1.

the percentage of syndiotacticity in the final polymer [29]. There was no discernible trend for the BC2 catalyst, and the percentage of syndiotacticity for polymers synthesized at ambient temperature, i.e., BC2S2 sample, was the lowest (53.5%), while the values for polymers produced at 50 °C and 70 °C, i.e., BC2T5 and BC2T7 samples, were 59% and 58%, respectively (Table 4).

Branching determination

^{1}H NMR analysis was also used to determine the branching density (the total number of branches per 1000 carbons) for homopolymers and copolymers, and the number of branches was calculated using equation 1 [21,30,31]:

$$\text{Total number of branches per 1000 carbons}=\frac{2(I_{CH_3})}{3(I_{CH_3}+I_{CH_2+\mathrm{CH}})}\times 1000 \qquad (1)$$

Where I_{CH_3} is the integral corresponding to the peak of methyl and butyl branches seen in the range of 0.7 ppm to 0.9 ppm, and $I_{CH_3}+I_{CH_2+CH}$ is the sum of the integrals of all peaks in the spectrum of produced polymers. Tables 5 shows the results of determining the branching density of homopolymers synthesized with the two catalysts. The high branching of the synthesized polymers suggests that the majority of insertions is made via substitutions 1 and 2. The polymer chain branches areas are a result of the substitutions of 1 and 2 followed by chain walking. The substitutions of 1 and 2 followed by chain walking result in chain linearization via metal center migration to the terminal carbon atom [21,32-34]. PMMA with the highest degree of branching was obtained with the BC2 catalyst at room temperature. At higher polymerization temperatures, the BC1 catalyst produced homopolymers with less branching.

Copolymers characterization

The mole fraction of comonomers in the synthesized copolymers was calculated using ^{1}H NMR studies (Table 6), (for the ^{1}H NMR spectra of the copolymers, see Figures S12-S14 in SI). To accomplish this, the chemical shift of the peaks in the spectrum corresponding to each comonomer must be determined, and then the percentage of the corresponding comonomers is calculated based on the surface area under each peak. The peaks in the range of 0 to 2.2 ppm correspond to the protons of 1-hexene and MMA. Except for the protons of the methoxy group, this region contains information about the total olefinic protons that contributed to the copolymer structure. If *A* and *B* are the regions under the peaks of 3.7 ppm and 0-2.2 ppm, respectively, the following equation (eq. 2) can be used to calculate the percentage of MMA monomer in the copolymer structure [18].

$$\text{MMA incorporation} = \frac{A/3}{\frac{A}{3}+[B-5(\frac{A}{3})]/12} \qquad (2)$$

Where (A/3) is equivalent to the moles of MMA, and (B-5A/3)/12 is equivalent to the moles of 1-hexene [21]. The calculated results showed that increasing the concentration of MMA comonomer in the feed increased the polar comonomer incorporation in the copolymer structure (Table 6). Brookhart and Xisheng Fu research groups separately found that increasing the concentration of methyl acrylate monomer in ethylene/MMA copolymerization using different palladium-diimine catalytic systems increased the cooperativity of polar comonomer in the polymer chain [35,36]. Moreover, Bagherabadi *et al.,* also studied copolymerization of 1-hexene and MMA using monocenter and bicenter nickel catalytic systems, as

Table 6. Results of branching rate of the copolymers synthesized using MMAO/BC1 catalytic system.

Sample code	1-Hexene (mmol)	Methyl methacrylate monomer (mmol)	Polar monomer corporation (%)	Branching density (CH_3/1000 C)
CO_1	75	25	65	192
CO_2	50	50	70	245
CO_3	25	75	73	231
CO_5	10	90	80	223

Polymerization conditions are according to Figure 2.

the concentration of MMA monomer increased, the incorporation of the polar comonomer in the polymer chain increased greatly; bicenter catalysts produced the highest incorporation of MMA in the chain. The presence of a second center in bicenter catalysts raises the local concentration of the polar monomer around the active centers, making the monomer more accessible [21].

Examining the branching density for the copolymers produced with the BC1 catalyst revealed an increasing trend with the increase of the polar monomer in the final copolymer structure and the ratio of monomers with the highest branching. The lowest amount of branching density for the produced copolymer, on the other hand, was obtained with the least amount of the polar monomer. Zohuri's team reported that in the copolymers produced with bulky monocenter catalyst, increasing the share of polar monomers in the copolymerization decreased the amount of branching, whereas no specific trend was observed in the copolymers produced with the bicenter catalysts; they also considered the obtained branch density values to be dependent on the type of substitution and also the increase or decrease in the chain walking mechanism [21].

Determination of molecular weight

GPC analysis was performed on one of the homopolymers synthesized with the BC1 catalyst (at ambient temperature), and the average molecular weight and molecular weight distribution were found to be around 4.5×10^5 g/mol and 2.9, respectively. The high molecular weight obtained in the produced polymer is most likely due to the presence of bulky substituents in the ortho-aryl position, which prevent chain transfer reactions and increase the diffusion rate, resulting in the production of PMMA with a high molecular weight [37,15].

CONCLUSION

Cobalt diimine bicenter catalysts were synthesized, identified and used for the polymerization of MMA and 1-hexene. The catalyst with 2,3,5,6-tetramethylbenzene-1,4-diamine bridge (BC1) showed the higher activity than other catalysts in the homopolymerization of monomers, and it was used in copolymerization, and the incorporation of polar monomers ranged from 65 to 80%. At the higher polymerization temperatures, the catalyst with 4,4-methylenedianiline bridge (BC2) demonstrated better thermal stability. The spatial order of the obtained homopolymers revealed a relatively high amount of syndiotacticity (up to 59%). However, as the polymerization temperature increased from 27 to 60°C, the amount of syndiotacticity for the polymer obtained by using the BC1 catalyst decreased. For the polymer produced by the BC2 catalyst, this trend increased until it reached 50°C and then decreased. The amount of branching in the resulting homopolymers ranged from 201-249 per a thousand carbons depending on the polymerization conditions, and at ambient temperature the most branching was obtained. Furthermore, at this temperature, the polymer obtained by the BC2 catalyst generated the highest branching content. Examining the branching density for the produced copolymers revealed an increasing trend with the increasing of polar monomer in the final copolymer structure, and a copolymer was prepared in an equal proportion of monomers with the most branching.

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CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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