

Polymerization of methyl methacrylate using bis(imine) cobalt, a polyolefin catalyst

Majedah Maroofi¹, Gholam Hossein Zohuri^{1,*}, Saeid Ahmadjo², Navid Ramezani¹

¹Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, P.O. Box 91775, Mashhad, Iran

²Department of Engineering, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran

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ABSTRACT

A mono-nuclear catalyst of bis-imine cobalt (MC) was synthesized with using 2,6-dibenzhydryl-4-ethoxy phenyl as a ligand. The so huge ligand was prepared via the reaction of 2,6-dibenzhydryl-4-ethoxy phenyl)-N=(CH₃)-C(CH₃)=O with diacetyl with equal mole stoichiometry in presence of formic acid catalysis. The catalyst was synthesized via a reaction between the ligands and cobalt salt (CoCl₂). The catalyst was used for polymerization of methyl methacrylate (MMA), (a polar monomer) in the presence of modified methylaluminoxane (MMAO). The highest polymerization activity (8.6 g PMMA/mmol cat. h) was obtained at [cocatalyst]/[catalyst]=1000:1 molar ratio and at room temperature reaction. For the prepared PMMA, Polymer with branching density of 263/1000C was obtained using ¹H NMR technique calculation. The microstructure of one of the produced PMMA was as follow: 48% syndiotactic, 29% isotactic and 23% atactic. GPC analysis of the polymer showed a number average molecular weight of about 5.7×10^5 g/mol and a narrow molecular weight distribution of 1.57. **Polyolefins J (2023) 10: 79-88**

Keywords: Bis-imine cobalt catalysis; polymethyl methacrylate; polymerization; tacticity.

INTRODUCTION

Polyolefins are a large group of polymers consisting of a great number of widely used polymers including polyethylene, polypropylene, polymers with longer chain olefins and their copolymers. Over the years, the polyolefin industrial production has grown and advanced remarkably in step with the rising global demand for such thermoplastics [1, 2]. From the pro-

duction point of view, the main driver of industrial developments in the production of polyolefins has been the rapid advancement of catalytic systems. Following to Karl Ziegler's discovery of coordination polymerization in 1950s, this approach to polymerization, which later became known as the Ziegler-Natta catalytic system, was found to have interesting features that

* Corresponding Author - E-mail: zohuri@um.ac.ir

greatly benefit the polymerization of ethylene, propylene and their co-polymers [3, 4]. A few decades later, with the discovery of methylaluminoxane (MAO) by Kaminsky, metallocene catalysts were found to have a remarkable capacity to facilitate copolymerization systems [5, 6]. With the advent of the late transition metal catalysts, this group of catalysts was found to be greatly benefit of polymerization of polar monomers and their copolymerization with olefinic monomers, becoming the subject of many studies related on regulation of molecular weight, molecular weight distribution, branching distribution and chain transfer in olefin polymerization [7-11]. The first case of olefin polymerization with late transition metal catalysts was reported in 1996 by Brookhart et al., who showed that Ni and Pd-based catalysts that contain bulky α -diimine ligands can produce high molecular weight polyolefins [12]. Some design structures based on electronic/steric modulation of ligands in catalysts have emerged, which can be produced suitable catalyst for olefin-polar monomer incorporation [13-17]. Despite the numerous beneficial features of Ni and Pd-based catalysts, they also have certain limitations, including poor thermal stability at high temperatures, which is crucial for industrial applications [18,19]. In 2017, Kimiaghali et al. synthesized two mononuclear Ni and Pd-based catalysts and investigated whether they can be used for polymerization of ethylene. The synthesized Ni catalyst with heat resistance up to 90°C and the synthesized Pd catalyst could remain active in temperatures of up to 80°C. Morphological examinations of the polyethylene and the catalyst samples showed that both synthesized Pd catalyst and the polymer samples produced from this catalyst are spherical [20, 21]. In a study by Khoshafat et al., they synthesized and used two Ni-based mononuclear and dinuclear diimine catalysts for polymerization of ethylene. While their mononuclear catalyst was somewhat poor in terms of activity, their dinuclear catalyst showed good results in terms of activity and molecular weight distribution, which can be attributed to the catalyst's dinuclearity and the electronic and spatial effects of substitutions on the main skeleton on ortho and para positions of the phenyl rings of the ligand used in the catalyst structure [22].

There are some reports on the polymerization of

1-hexene with different types of catalysts, in this regard, the branching topology of poly(1-hexene) with a dual catalytic system by Maddah et al. revealed that long-chain branches are formed with incorporation of the in situ produced macromers. By repetitive transfer of the growing chains to the chain transfer agent and replacement by the second catalyst, a branch-on-branch structure was formed. The creation of extensively branched structures were simply reflected in the rheological behavior [23].

A unique feature of the late transition metal catalysts is that they can produce branched polyethylene without α -olefin comonomers. Also, they are able to polymerize polar and non-polar monomers that are extremely important in the industry. In 2018, Avar et al. investigated the copolymerization of 1-hexene with polar monomers such as butyl acrylate and methyl methacrylate at ambient temperature with 1, 4-bis(2,6-diisopropylphenyl) acenaphthene-diimine-nickel (II) dibromide as a catalyst, while, diethylaluminum chloride (DEAC) and ethylaluminumsesquichloride (EASC) were used as cocatalysts [24]. Similarly, in 2019, Kanai et al. studied the polymerization and copolymerization of ethylene with polar monomers including methyl 10-undecenoate, 10-undecenoic acid, 11-chloroundecene, and 5-hexen-1-ol using nickel catalysts [25]. Copolymerization of 1-hexene with methyl methacrylate (MMA) using both a mononuclear and dinuclear Ni-based α -diimine catalysts were investigated by Bagharabadi et al. [26]. The results showed that, the presence of two metal centers in the dinuclear catalyst increased the optimal cocatalyst-to-catalyst ratio and also enhances the activity of the catalyst in the synthesis of PMMA; this effect can be attributed to participation of the two active centers in the polymerization. The synthesized PMMA led to the production of high amounts of atactic polymer. Wang et al. investigated the polymerization of MMA with MAO-activated Pd-based β -ketoiminato complexes as highly active catalysts and examined the effects of polymerization factors such as, temperature, catalyst-to-cocatalyst ratio, and polymerization time on the activity of catalysts. Their structural analysis of the synthesized PMMA showed that the produced polymer has moderate syndiotactic microstructures [27]. Su et al., synthesized a number of mono(imino)pyr-

role ligands and their Ni complexes by new methods such as microwave irradiation and investigated their use for MMA polymerization. All their catalysts had average activity in the range of 35-47 (gPMMA/mmol Ni. h). These researchers reported that the catalyst performance was influenced by the ligand structure, polymerization time, and temperature [28]. Over the years, a large number of Ni and Pd-based transition metal complexes with α -diimine ligands have been synthesized and used for the polymerization and oligomerization of α -olefins. However, there are very few reports on cobalt (Co) complexes with this type of ligands and their use in MMA polymerization. To fill this gap, this study investigated the polymerization of MMA with a cobalt-based catalyst with 2,6-dibenzhydryl-4-ethoxy phenyl ligand (MN), and the effect of the synthesized catalyst on the polymer microstructure was also studied.

EXPERIMENTAL

Materials

The required compounds including para-ethoxyaniline 97%, diphenyl methanol (benzhydryl) 98%, aniline, diacetyl 97%, formic acid, para-toluene sulfonic acid, and cobalt (II) chloride were all acquired from Merck. All solvents including methane dichloride, toluene, and diethyl ether were distilled and dried with calcium hydride. The required monomers were distilled under conventional distillation driers and stored on activated molecular sieve (4A/13x).

Polymerization

The polymerization of MMA and 1-hexene was performed in a 100 mL two-neck round-bottom flask, whose contents of which could be mixed by a magnetic stirrer. The flask temperature was controlled by a water bath at ambient temperature. To polymerize MMA, dry toluene (6 mL) was placed inside the reactor under a neutral atmosphere and the flask was placed under argon gas and vacuum three times to remove all moisture and impurities. The monomer (10 mL) and after a few minutes the required amount of modified methylaluminoxane (the cocatalyst) were injected into the reactor while stirring. Finally, the

synthesized catalyst (4 μ mol) dissolved in toluene (4 mL) was added to the reactor to start the polymerization. The reaction was stopped after the required polymerization time and the resulting solution was added to a flask containing acidic methanol (5%) to allow the polymer to precipitate. The produced polymer was then dried in a vacuum desiccator and weighed.

Characterization of polymers

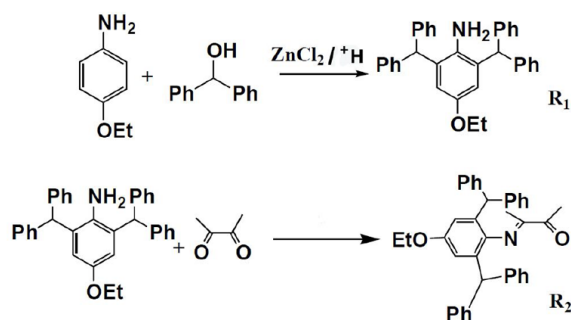
The functional groups in the ligand, the catalyst and the polymer itself were identified with infrared (IR) spectroscopy. This spectroscopy was performed with an AVATAR 370A FTIR spectroscopy machine manufactured by Thermo Nicolet, at the Ferdowsi University of Mashhad. The molecular weight of polymers was measured using gel permeation chromatography with an Agilent-1100 GPC, at Iran Polymer and Petrochemical Institute. For this measurement, appropriate amounts of polymers were dissolved in dry tetrahydrofuran and injected into the column in room temperature. Proton nuclear magnetic resonance (^1H NMR) spectroscopy was used to identify the synthesized ligands and the obtained polymers and copolymers and also to determine the tacticity of the polymers. This spectroscopy was performed with a Bruker AC 300 NMR spectrometer in room temperature at Bu-Ali Research Institute in Mashhad with deuterated chloroform used as the solvent.

RESULTS AND DISCUSSION

Ligand and catalyst synthesis

Synthesis of the $\{(2,6\text{-dibenzhydryl-4-ethoxy phenyl})\text{-N}=\text{C}(\text{CH}_3)\text{-C}(\text{CH}_3)=\text{O}\}$ (R2) ligand

The R1 ligand was synthesized through the reaction of para-ethoxyaniline with diphenyl methanol with a 1:2 mole ratio (aniline to alcohol) according to Scheme 1. In the FTIR spectrum of the synthesized R1 ligand, i.e., 2,6-bis(diphenylmethyl)-4-ethoxyaniline (Figure 1), symmetric and asymmetric stretching bands around 3358 and 3426 cm^{-1} are related to NH_2 amino group. The absorption band at 1293 cm^{-1} is related to the stretching vibration of the ethereal C-O bond. The absence of the OH peak related to diphenyl methanol confirms the synthesis of the desired compound,



Scheme 1. Synthesis route of the R1 and R2 ligands.

and the peaks appearing in the 1600–2000 cm^{-1} region confirm the formation of polysubstituted rings next to mono substituted rings [19].

The R2 ligand was synthesized according to previously published instructions [19,23]. A summarized description of the synthesis method is as follows. Diacetyl (3.45 mmol, 0.3 mL), methanol (30 mL) and a small amount of formic acid as catalyst were placed in a 100 mL flask and gradually added to the synthesized amine (R1) (according to Scheme 1) i.e., 2,6-bis(diphenylmethyl)-4-ethoxyphenyl (3.12 mmol, 1.5 g). The resulting solution was stirred for four days. The completion of the reaction was certified by TLC method. The resulting yellow precipitate was filtrated and dried (R2) (Scheme 1).

The FTIR spectrum of the R2 ligand showed a sharp peak of C=O at 1701 cm^{-1} and a peak at 1650 cm^{-1} , which indicates the existence of the C=N bond. The absence of the stretching bands of the NH_2 amino group indicates that the desired compound has been synthesized (Figure 2).

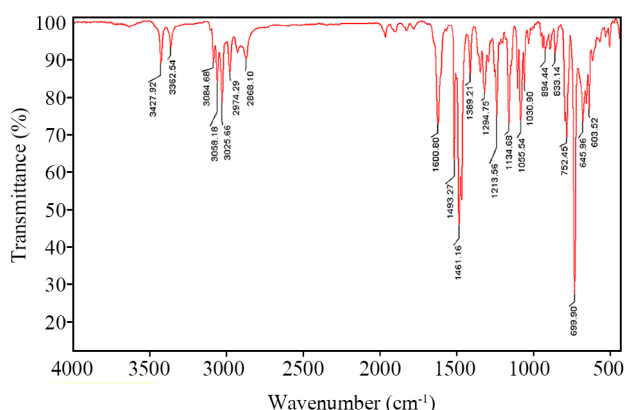


Figure 1. FTIR spectrum of 2,6-bis(diphenylmethyl)-4-ethoxyaniline compound (R1).

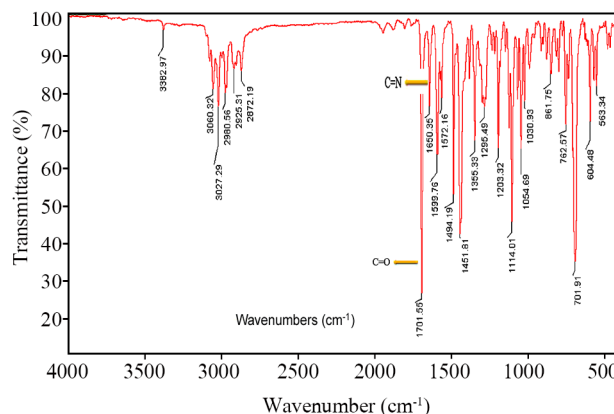


Figure 2. FTIR spectrum of the R2 ligand

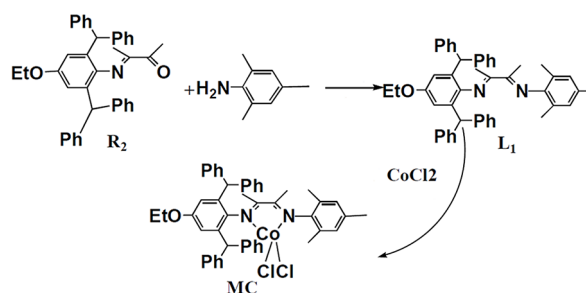
Synthesis of the L1 ligand

For synthesis of the L1 ligand, the R2 ligand (0.5 g) was added to toluene (50 mL) and then 2,4,6-trimethylaniline (0.21 g) was added while stirring in the presence of *para*-toluenesulfonic acid catalyst. The Dean-Stark apparatus was used to remove the existing water as reflux so that the reaction could proceed to its highest level. Precipitation was then obtained via addition normal hexane. The obtained precipitate was separated and washed with normal hexane for further purification. The synthesis route of the L1 ligand is provided in Scheme 2. To prepare the catalyst, the L1 ligand was added to cobalt chloride.

FTIR was used to confirm the structure of the prepared ligand. The results of this analysis are plotted in Figure 3. As can be seen, the carbonyl peak in the initial R2 compound (1701 cm^{-1}) is completely absent and the 1639 cm^{-1} peak related to the C=N vibration is more pronounced, indicating that the reaction has occurred as intended.

Synthesis of the mononuclear cobalt catalyst (MC)

The catalyst was synthesized under a neutral atmo-



Scheme 2. Synthesis route of the L1 ligand and the catalyst.

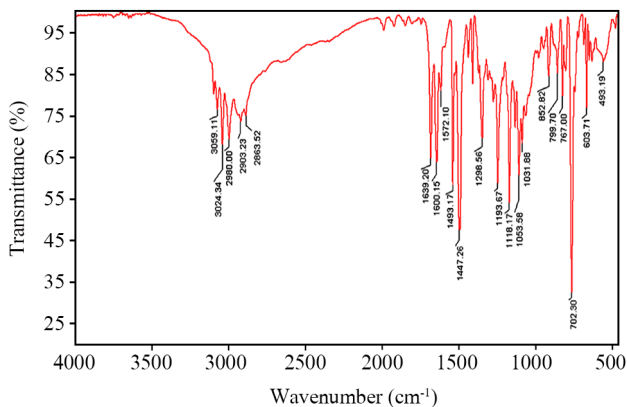


Figure 3. FTIR spectrum of the L1 ligand.

sphere and inside a glovebox. For this synthesis, a solution of the L1 ligand (0.05 g) (Scheme 2) was prepared in dry dichloromethane (10 mL) and added dropwise to a 50 mL flask containing a solution of cobalt (II) chloride (0.01 g) in dichloromethane (25 mL). The mixture was then stirred at room temperature. The resulting precipitate was washed with diethyl ether and dried. The synthesis route of the MN catalyst is given in Scheme 2. The FTIR spectrum of the synthesized catalyst (for the 200-700 cm^{-1} region) is shown in Figure 4. The absorption band at 280 cm^{-1} is related to the vibration of the Co-N bond and the one at 1300 cm^{-1} is related to the vibration of the Co-Cl bond (not shown here) [29]. These results confirm the formation of the target complex (Figure 4).

Activity of the mononuclear MN catalyst for the MMA monomer

The mononuclear MN catalyst was used in the polymerization of MMA, a polar monomer, in the presence of MMAO which used as a cocatalyst, and the effect

of the cocatalyst-to-catalyst ratio at ambient temperature was investigated. The results of this investigation are presented in Table 1. As the results show, the highest catalyst activity was achieved at the cocatalyst-to-catalyst ratio of 1000:1. The polymerization temperature was not further examined because, unfortunately, the catalyst activity was somewhat poor at higher polymerization temperatures, may be due to asymmetrical structure or steric effect of synthesized catalyst. On the other way, electron-withdrawing substituent in synthesized catalyst will make the catalyst susceptible to degradation, resulting in reduced stability and polymerization activity at higher polymerization temperature. Pan et al. synthesized a (imino) pyrrole-based Ni complexes and used them for MMA polymerization. All their catalysts had average activity in the range of 35-47 (gPMMA /mmol Ni.h). They reported that the catalysts performances were influenced by the ligand structures, Al/Ni ratio and polymerization temperature [28].

Actually, the multinuclear synergistic effect and bimetallic catalysts increased activity and thermal stability as previously reported [18,22,23,30]. Vinyl-terminated HDPE was produced by mono and binuclear cobalt catalysts by Rahimpour et al., the later catalyst showed the higher activity and high temperature stability in comparison to mononuclear catalyst, and the maximum activity of binuclear catalyst could be obtained at [Al]/[Co] molar ratio of 2000:1 [31]. In another approach, the binuclear cobalt-based catalysts containing bis(phenyl) bridge between centers have been prepared by W.H. Sun et al., whose activity, thermal stability, and lifetime where reported to be higher than the corresponding mononuclear analogs [32].

Structural properties of the synthesized polymers

The FTIR spectrum of the polymethyl methacrylate

Table 1. MMA polymerization using the MN/MMAO catalytic system.

Sample	[Al]/[Co] ratio	Weight (g)	Activity (g PMMA/mmol cat.h)
M.N ₁	500	0.18	2.3
M.N ₂	1000	0.66	8.6
M.N ₃	1500	0.6	7.8

Polymerization conditions: catalyst 3 μmol , methyl methacrylate monomer 10 mL, reaction temperature 27°C, reaction time 24 hours, toluene solvent 10 mL

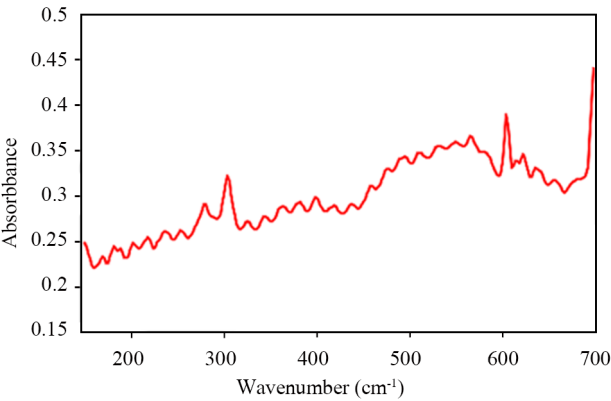


Figure 4. FTIR spectrum of the MC catalyst.

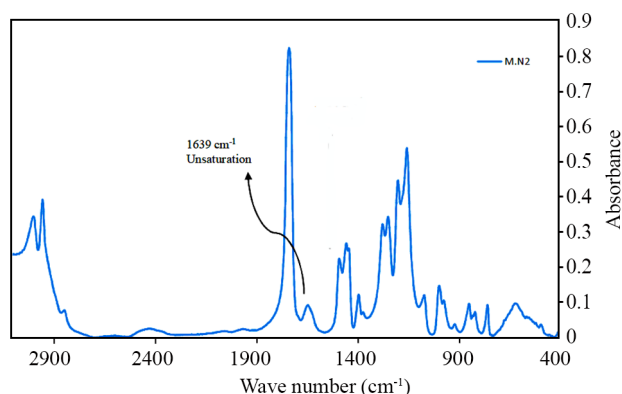


Figure 5. FTIR spectrum of polymethyl methacrylate synthesized with the MC catalyst. Polymerization conditions: as indicated in Table 1 for the sample M.N₂.

(PMMA) obtained from the synthesized catalyst (Figure 5) is indicative of relatively high unsaturation and linearity in the polymer obtained from the MN catalyst. The peaks in the 2850-3000 cm⁻¹ region are related to the stretching vibration of C-H, the peak in the 1452 cm⁻¹ region is related to the bending vibration of CH₂, and the one in the 1360-1389 cm⁻¹ region is related to the bending vibration of CH₃ in the polymer. The peaks in the 1000-1200 cm⁻¹ region are related to the stretching vibration of the C-O bond, and the peak at 1731 cm⁻¹ belongs to the vibration of the carbonyl bond, confirming the presence of MMA in the produced polymer [33].

Using nuclear magnetic resonance spectroscopy, one can examine the tacticity, branching, and general microstructure of the synthesized polymers. Figure 6 shows the ¹H NMR spectrum of a sample of polymethyl methacrylate synthesized with the MN catalyst. The index peak at 3.6 is related to the protons at-

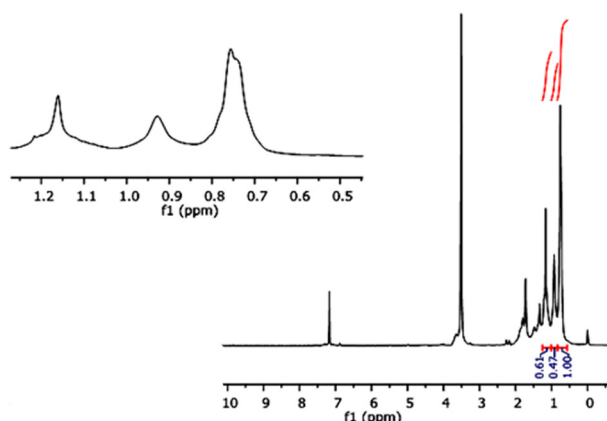


Figure 6. ¹H NMR spectrum of polymethyl methacrylate synthesized with the MC catalyst. Polymerization conditions: as indicated in Table 1 for the sample M.N₂.

tached to the methoxymethyl methacrylate group [34], which indicates the correct synthesis of this polymer. Also, the peak in the 4.5-7 region is related to the C=C double bond.

Tacticity analysis

The ¹H NMR spectrum of polymethyl methacrylate shows three peaks in the 0.85-1.25, 1.60-1.90 ppm regions and at 3.60 ppm, (expanded area in Figure 6) which correspond to the protons of -CH₃ from-C(CH₃)(COOCH₃), -CH₂-, and -OCH₃ respectively. The polymer tacticity in terms of syndiotactic [rr], isotactic [mm], and atactic [mr] ratios can be determined by examining the triple peaks of alpha-methyl (α-CH₃) and obtaining the surface integral of the desired peaks [26,35-36].

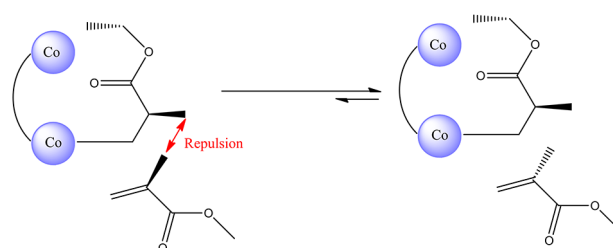
The tacticity of the sample M.N₂ in Table 1 was calculated by the following formulas (Figure 6):

$$(\text{Syndiotacticratio}) \quad rr\% = \frac{\int rr}{\int rr + \int mr + \int mm}$$

$$(\text{Atacticratio}) \quad mr\% = \frac{\int mr}{\int rr + \int mr + \int mm}$$

$$(\text{Isotacticratio}) \quad mm\% = \frac{\int mm}{\int rr + \int mr + \int mm}$$

In terms of tacticity, polymethyl methacrylate obtained with the MN catalyst was determined to be 48% syndiotactic, 29% isotactic, and 23% atactic. This high syndiotacticity can be related to the repulsion between the α-methyl group in the monomer and the catalyst as indicated in Scheme 3 [26]. MMA polymerization using the mononuclear α-diimine nickel catalyst with less steric hindrance reported by Zohuri et al., which the higher atactic content of the produced PMMA may be due to the structure of catalyst [26]. However Abedini et al., used camphyl-based nickel catalyst with higher, steric hindrance, which they could produce polymer with higher syndiotactic content [35]. In another way, Wang et al., investigated the polymerization of MMA with MAO-activated Pd-based β-ketoiminato com-



Scheme 3. Potential interactions of the α-methyl MMA group.

plexes, which the synthesized PMMA showed the moderate syndiotactic microstructures [27]. It can be concluded that the spatial structure of the catalyst can affect the tacticity of the polymer.

Branching analysis

The synthesized polymer's branching density (total number of branches per 1000 carbons) was determined by using the results of the ^1H NMR analysis according to the following formula [26,37,38].

$$\text{Total number of branches per 1000 carbons} = \frac{2(I_{\text{CH}_3})}{3(I_{\text{CH}_3} + I_{\text{CH}_2} + I_{\text{CH}})} \times 1000$$

In this formula, I_{CH_3} is the surface integral of the peak of methyl and butyl branches, which is in the range of 0.74 to 0.88 ppm, and $I_{\text{CH}_3} + I_{\text{CH}_2} + I_{\text{CH}}$ is the sum of the surface integrals of all the peaks in the spectrum of the synthesized samples. The branching density of sample M.N₂ shown in Table 1, was determined to be 263 per 1000 carbons, however branching densities for some PMMA produced by binuclear nickel catalysts were in the range of 80-217 per 1000 carbons that may related to the special structure of catalysts [26]. The high branching of the synthesized polymer indicates that most of the insertions have been of the 1,2-insertion type, which when followed by chain straightening, leads to the branching of the polymer chain. This kind of insertion in combination with chain straightening leads to the linearization of the chain by the migration of the metal center to the terminal carbon atom [26, 39-41].

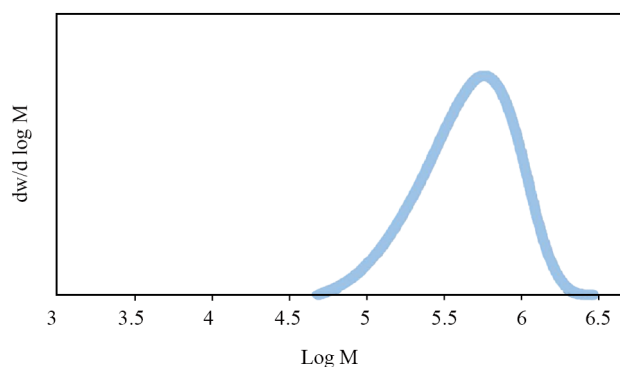


Figure 7. GPC diagrams of polymethyl methacrylate of sample M.N₃. Polymerization conditions: as indicated in Table 1 for sample M.N₃.

GPC analysis

The GPC analysis of sample M.N₃ from Table 1 showed that number average molecular weight of about 5.7×10^5 g/mol and the polymer exhibited a relatively narrow molecular weight distribution of 1.57 (Figure 7). The high molecular weight of the produced polymer is due to the presence of the substituents in the ortho-aryl position of the catalyst, which block the axial positions, thereby preventing chain transfer reactions and lowering the diffusion rate, leading to the production of high molecular weight polymethyl methacrylate [18, 26].

CONCLUSIONS

The cobalt α -diimine catalyst prepared with benzhydryl derived ligand framework was an active catalyst in methyl methacrylate polymerization. This catalyst activated with MMAO, could exhibit high activity up to 8.6 g PMMA/mmolcat.h. The produced poly (methylmethacrylate) sample exhibited narrow polydispersity ($\text{PDI} = 1.57$), high molecular weight (5.7×10^5 g.mol⁻¹) and 263 branches/1000 C. The tacticity of the poly (methyl methacrylate) was composed of 48% syndiotactic, 23% atactic, and 29% isotactic.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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