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SYNTHESIS OF POLYETHYLENE WITH α -DIIMINE NICKEL COMPLEXE

A graduation research project
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الشكر الخاص أولاً لله على فضله وتوفيقه،
ثم والداي حفظهم الله، وهذه ثمرة من ثمار غرسكم.

إلى الذين مهدوا لنا طريق العلم والمعرفة، إلى جميع أساتذتنا الأفاضل.
إلى من وقف وساهم وسعى وقدم لنا العون في إنجاز هذا البحث بجهودهم الكبيرة

د. سلطان الشميمري
م. عدي الزامل
أ. دخيل الله المطيري
أ. محمد واصلي

وجميع من كان عوناً لي
شكراً لكم.

Abstract

An α -diimine nickel complex was synthesized from the reaction of 2-aminobiphenyl and 3-butanedione then interacted with nickel (II) bromide. The complex was used to polymerize ethylene with different reaction conditions to study the effect on the catalytic activity. The reaction pressure was varied between 1 to 7 bar and find that the activity maximized when the reaction pressure was set to 3 bar. For the polymerization temperature in the range 10 to 70 °C, the activity was maximized at 30 °C.

1. Introduction

Polymer is found in our lives before it has been discovered. It could be found naturally in human bodies, in plants and animals. Rubber has been found in plants in the early of 1800s. Today it becomes one of the largest commercial industries, plastic was the first commercial manufacturing of polyethylene materials made by human, it was discovered in 1846 by Schonbein of Switzerland¹. Polymer in general is a compound that contains repeating small molecules which is called monomer. It is also can be found in a form of oligomers where the chain contains a few number of monomer ². Polymer structure can be divided into three main forms; linear polymer chain, branched of linear chain, or cross-linked (network) polymers as shown in figure 1.

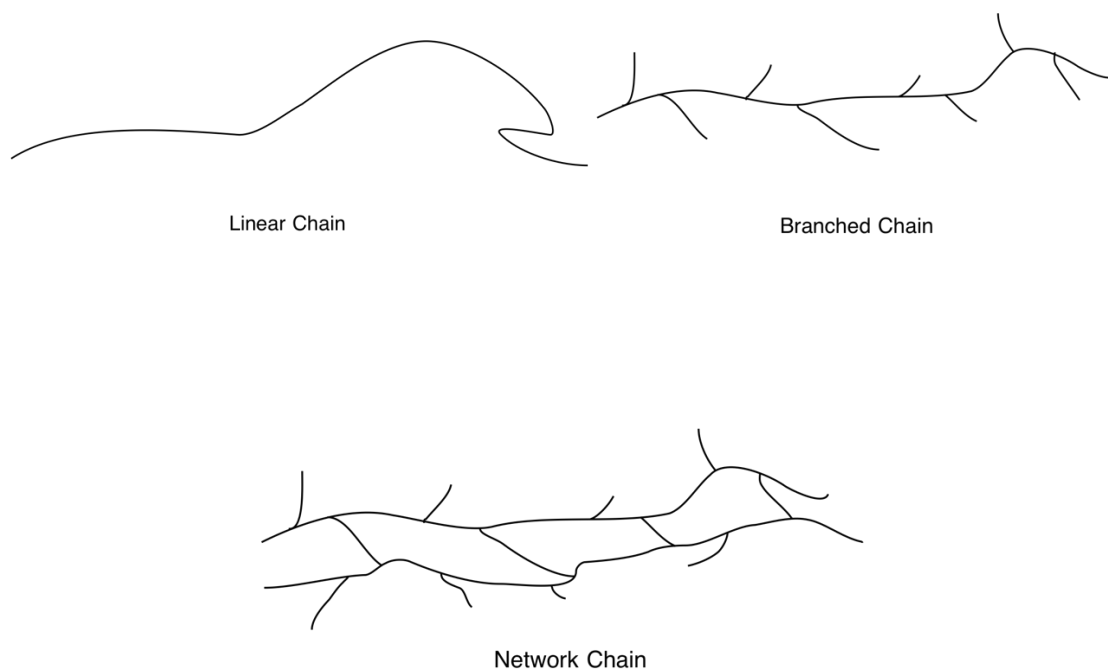


Figure 1: Structure of polymers¹

Polymers can be divided into two type, homopolymer which consists of only one type of monomer in the same polymer chain. Contrary in copolymer consisting of two or more monomers linked in the same polymer chain. The arrangement of the monomer in copolymer can be tail-to-tail, tail-to-head, or head-to-head. Therefore, copolymers can be classified on how to the arrangement of repeating units in chain, alternating copolymer, random copolymer, block copolymer, and graft copolymer³ see figure (2).

A common polymer today is polyethylene (PE), It was discovered in 1933, and the capacity of polyethylene globally in 2008 amounted to more than 93 million tons, then in 2015 has an increased rate to 44%⁵. Work on polyethylene started "Gibson and Fawcett" in March 1933, when they found that a white waxy substance, it was produced when ethylene and benzaldehyde compressed to 1900 bar and heated to 170 °C producing partially crystalline polyethylene. The first production and the patent was in 1936, and due to high temperature and side reactions occurred and formed branches and the density found between 915 – 925 kg m⁻³⁶.

Polyethylene have been divided into three main groups based on the density and structure. Low-density polyethylene (LDPE) which has long- and short-chain branches, 15 to 30 short-chain branch (SCBs) every 1000 carbons and the density 910 to 925 kg m⁻³, and the typical degree of crystallinity is less then 50%. High-density polyethylene (HDPE) has small branches, counted to be less than 10 small branches every 1000 carbons and the density 941 kg m⁻³ or above and the typical degree of crystallinity is 70% or more, due to the absence of LCBs. Lastly, linear low-density polyethylene (LLDPE), which has small branches, branches very tight depending on the monomer used with ethylene and the density 920 and 940 kg m⁻³ and the typical degree of crystallinity around 40%^{6,7}. See Figure 3.

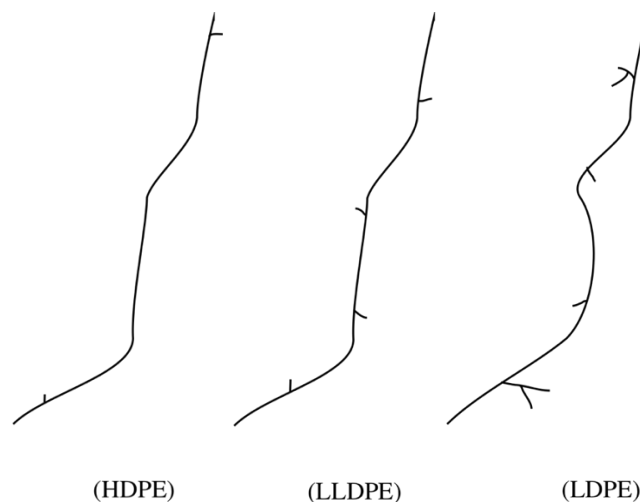


Figure 3: Types of Polyethylene⁷.

2. Background

Free radical polymerization is the production of a low-density polyethylene (LDPE)⁶. The presence of ethylene in liquid phase in the reaction due to high pressure and high temperature. The most popular initiators are peroxides and azo compounds. To start the chemical reaction, in the first step the initiator decomposition, “I” is initiator such as peroxide and “k_d” is decomposition rate constants, through this process two free radicals are generated “2R•”. In the second step, the initiator, the primary radical “R•” reacts with a monomer “M” and “k_i” is the initiation rate constant. In reality, not all the primary radicals initiate the growth of polymer chains, because of some primary radicals initiate side reactions and are wasted, for this reason there is an initiation efficiency “f”. In the third step, propagation reactions are responsible for the chain growth process. In general, “P_r•” has a length of chain “r” and reacts with the “M” and gives “P_{r+1}•”. There are two types of termination reactions, Disproportionation termination and combination termination⁸. Figure 4

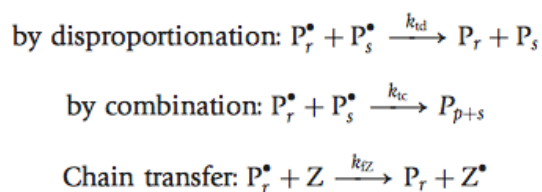


Figure 4 : Free radical polymerization ⁸

Chain transfer reactions occur to polymer radicals, and chain transfer agents are intentionally added for regulation of polymer molecular weight depending on the reaction. The molecule “Z” can be monomer, solvent, polymer, or some impurities. If “Z” is incapable of reacting with “M” or a retarder “Z” can be an inhibitor if “M” reacts with “Z” at a slower rate than propagation. An ideal chain transfer agent must have a rate constant similar to or larger than that of propagation “k_p”⁸. Figure 5

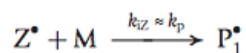


Figure 5: Chain transfer reaction ⁸

Ziegler-Natta catalyst was discovered in 1950 passed rapid developments in 1960s and in 1970s revolutionized the world of polymer industrial. The production of High-density polyethylene (HDPE) by Ziegler-Natta catalyst⁸. The transition metal component is usually either titanium or vanadium. The main group metal alkyl compound is usually aluminum alkyl, and in common the titanium component is called "catalyst" and the aluminum alkyl is called "co-catalysis"⁹.

Copolymerization of α -olefin and ethylene produced linear low density polyethylene (LLDPE), usually containing 1-butene, 1-hexene, or 1-octene by Ziegler-Natta catalyst⁹. Global consumption is increasingly impressive rates of LLDPE the search for more production and improve performance¹⁰. The properties LLDPE are affected by the polymerization of olefins to various factors, including a large molecular weight distribution and the distribution of the monomers, in return there are the natural properties of the catalyst and polymerization conditions¹⁰.

The development the polymerization process of ethylene and olefins depends on the early transition elements and lanthanide catalysts currently has subject to intensive study¹¹. The process of homogenous catalysts provides advanced technology to the traditional heterogeneous systems. Ziegler-Natta systems observation polymerization of mechanisms that can be obtained and use to control the changes in the microstructure of polymer properties. Although dominance early metal catalysts of polymerization processes in the industry, but that there is a tendency to lanthanide metal catalysts and have the ability to produce polymers different microstructure^{11, 12}. Currently, well-known catalysts based on complexes of cobalt, rhodium, nickel, palladium, platinum and iron. It has been prepared for the polymerization of olefins. Now focus on the work to develop olefins polymerization catalyst using α -diimine complexes of nickel and palladium of general structure¹¹. First work appeared in 1995, active catalysts maybe easily created and use by reaction of Ni II dibromide complex with methylaluminoxane (MAO)¹¹. Some research groups then, created closely catalyst systems of olefin polymerizations. These catalysts for polymerization of ethylene and olefins produce high molecular mass polymer with nickel and similar to early metal catalysts systems in terms of activity¹². Differences in microstructure and properties of polymers made using these nickel and palladium catalysts are observed and compared with those made using early metal Ziegler-Natta and Metallocene technology¹¹. For example, polyethylene prepared with nickel or palladium catalysts can form branched to largely linear polymer, and therefore characteristics

varied from soft to hard plastic. It was observed that polymer properties are generally depend on reaction conditions, ligand structure, and the metal ¹².

3. Experimental

Because of sensitivity to air and moisture, all reactions were performed in inert conditions. A glovebox system and Schlenk techniques (Schlenk line and Schlenk tubes) were used to run the reactions under nitrogen. All solvents used were purified using Anhydrous. Nickel dibromide was stored in the glovebox.

3.1. Ligand synthesis

As reported in the literature ¹³, in a 250 cm³ 2-necked flask and using Schlenk line, 2-aminobiphenyl (2.0361 g, 12 mmol), and 3-butanedione 0.5 ml (0.526 g, 6 mmol) were added. Then 35 ml of ethanol as a solvent and 0.4 ml of formic acid were added to the mixture. The mixture was stirred for 5 hours at 55 °C. It gave a yellowish powder, the powder was recrystallized from a mixed solvent of petroleum ether/ethyl acetate 1:1 to give yellow crystal, then filtered and dried to give a yield of (0.5 g, 19.5%). ¹H NMR (600 MHz, CDCl₃), δ 1.83 (6H, s, 13), δ 6.7 (2H, d, 6), δ 7.16-7.18 (2H, t, 5), δ 7.25-7.32 (10H, overlapped, aromatic), δ 7.36 (2H, t, 4), δ 7.38 (2H, d, 3).

3.2. Complex synthesis

As reported in the literature ¹⁴, the ligand crystal was moved to the glove box. In a 250 cm³ 3-necked flask the ligand (0.3018 g, 0.77 mmol), and nickel bromide (0.24 g, 0.77 mmol) were placed and dried 30 ml of (DCM) dichloromethane was added as solvent. The mixture was left stirring for 4 days. An orange solid was produced, it was dried to get orange powder, and recrystallized from DCM to give red-brown crystals.

3.3 Polymerization

3.3.1 Catalyst synthesis

In the glove box, complex was grinding with a stirrer to powder and dissolved with a small amount of DCM to a complete dissolving. It was then moved to a “Catalyst Feeding Cylinder” then topped up with distilled toluene. A number of different cylinder were prepared and used to polymerize ethylene.

3.3.2 Co-catalyst synthesis

In the glove box, (MAO) methylaluminoxane was added into “Co-catalyst Feeding Cylinder” and topped up with toluene. MAO was used with different Ni:MAO ratio, 1:2000 and 1:3000.

4. Discussion

4.1 Ligand Synthesis

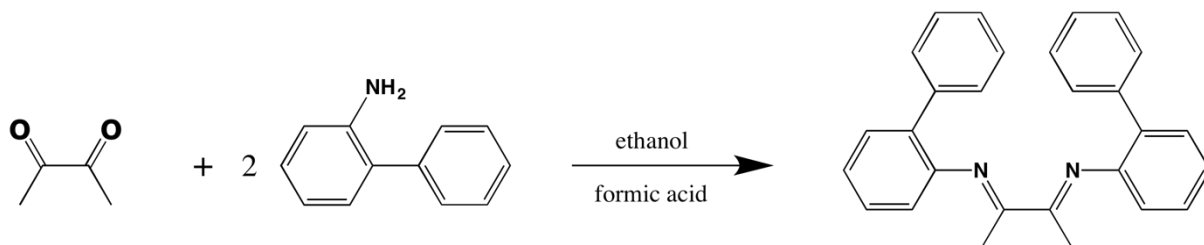


Figure 6: Synthesis of the ligand

The ligand was produced from the interaction between 3-butanedione and 2-aminobiphenyl in ethanol in the presence of formic acid as a catalyst, yellowish powder resulted after filtration and dried processes, the crystal was formed from a slow evaporation of the mixed solvent of petroleum ether/ethyl acetate to give crystal see Figure 7.

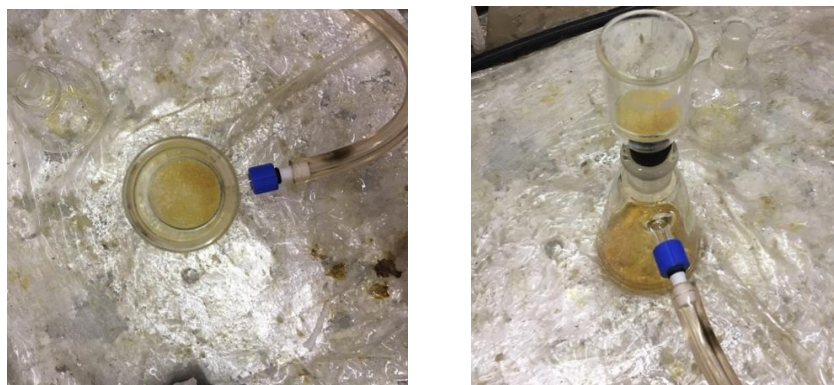


Figure 7: The ligand crystal

4.2 Complex Synthesis

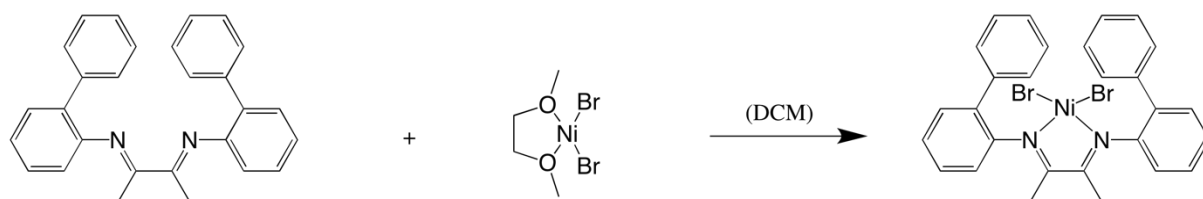


Figure 8: Synthesis of the complex

The complex is air and moisture sensitive, so the reaction was performed inside the glove box to assume that the reaction is not affected by O_2 or H_2O , performed under N_2 in the glove box to make sure that the reaction is not affected. The color produced complex was orange powder and then crystallized to give red-brown crystals. Due to the shortage of time and the lack of equipment, the complex was not characterized and the only proof of the success of the reaction is that the color of the ligand has changed from yellow crystals to red-brown crystals complex after the reaction with $NiBr_2(DME)$ as it was found by Gao *et. al.*¹⁵. The complex was recrystallized in three different ways, firstly was fast evaporation of (DCM) which has not been successful, the second attempt was by very slow evaporation which gives the best and large crystal. The third attempt was by Vapor Diffusion where a small tube contains small amount of the powder dissolved by DCM inside a larger tube containing hexane see Figure 9, the crystals produced by the third method was found to be smaller. Figure 9 and 10 show pictures and diagrams to explain all three methods.

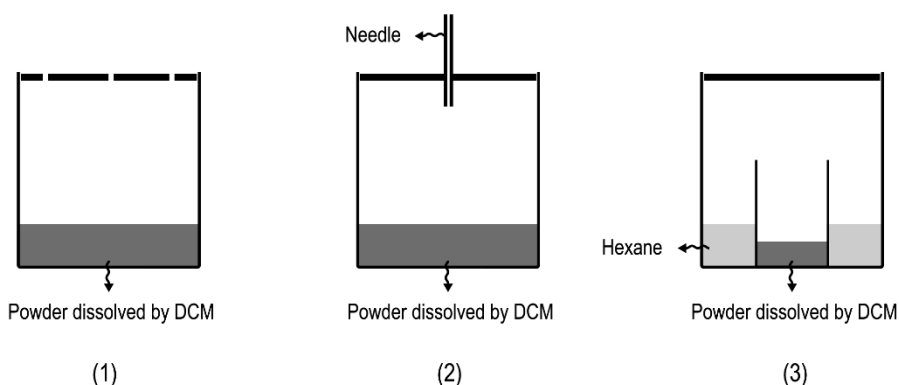


Figure 9: The three ways for crystallized for complex

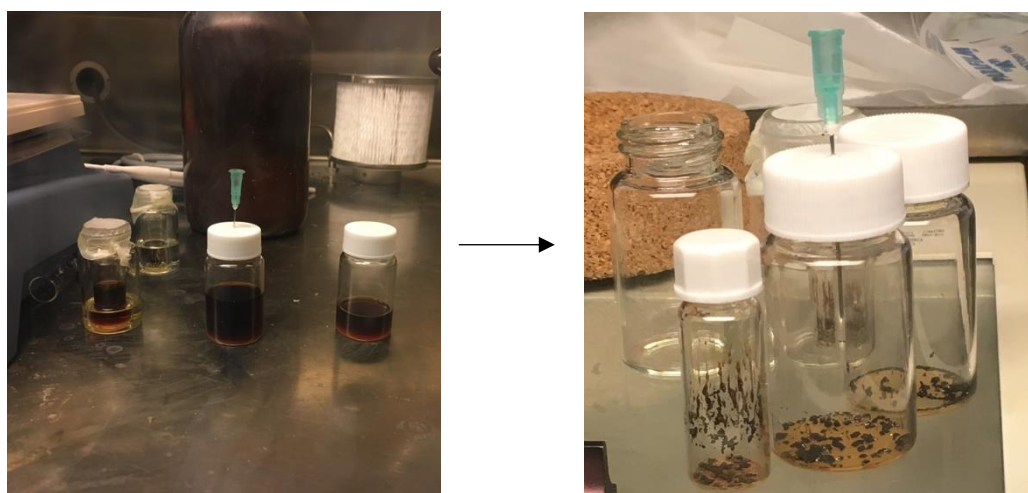


Figure 10: Crystallized for complex

4.3 ^1H NMR

The ^1H NMR spectra were recorded on a 600 MHz using CDCl_3 as solvent. Peak recorded in δ 1.83 (6H, s, 13) is methyl in 3-butanedione show in right due to very low electronegativity as shielded see figure 11. The shift of the peaks are clearly influenced by the aromatic attached to the N-aryl ring. For example, the doublet peaks around 7.37 ppm is responsible of H on carbon 3 (Figure 11), which has been shifted because of the effect of the *ortho*-substituents of N-aryl rings. Furthermore, the triplet peaks around 7.17 ppm and the doublet peaks around 6.7 ppm are related to Hs on carbon 5 and carbon 6, respectively.

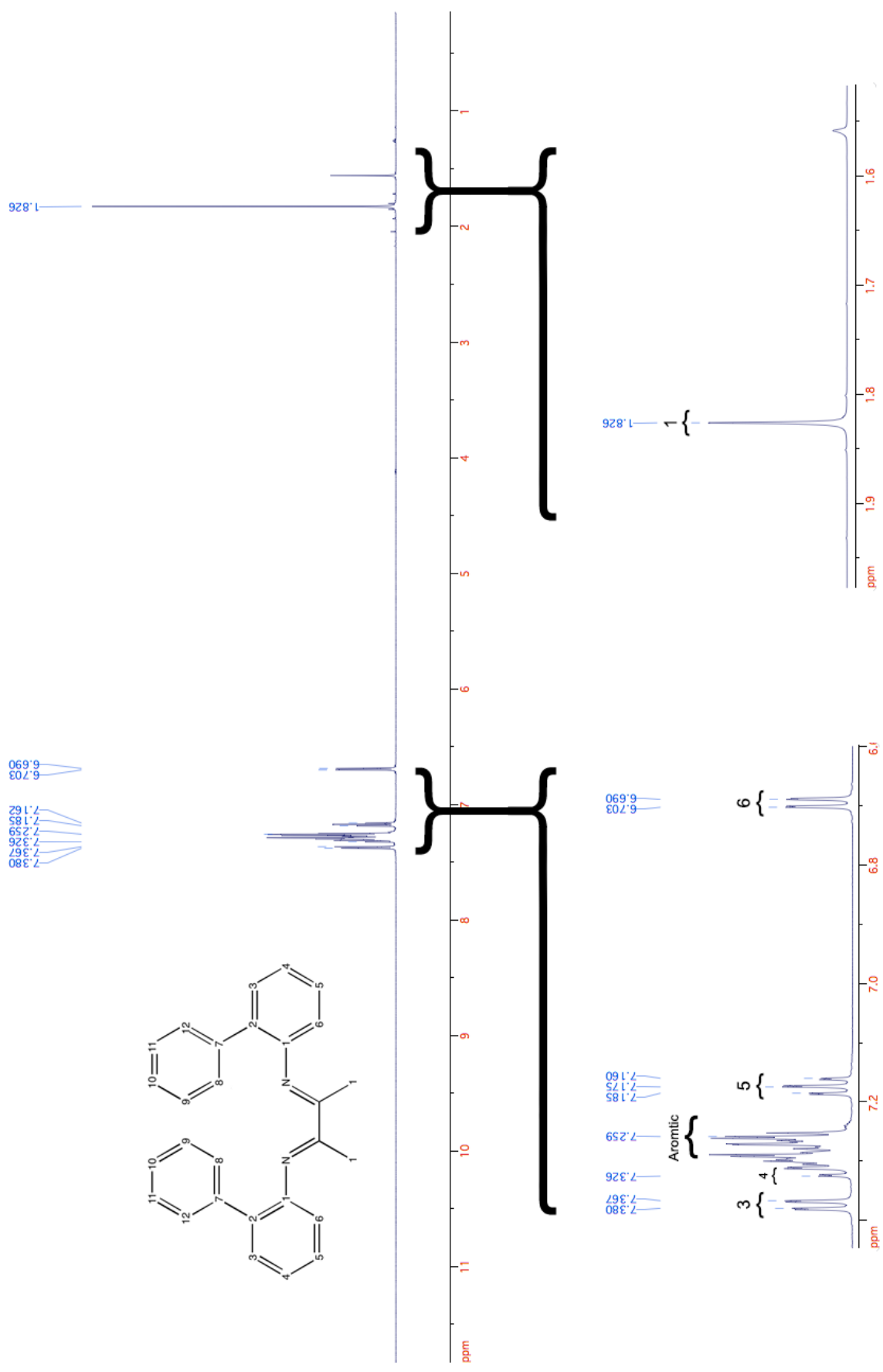


Figure 11: ^1H NMR spectrum

4.5 Polymerization

Table 1: Polymerization Data for Experiments

Entry	Catalyst (μmol)	Pressure (bar)	Temperature ($^{\circ}\text{C}$)	Yield (g)	Activity (kg PE) (mol^{-1}Ni) h^{-1}
1 ^a	20	3	30	50.5	10200
2	10	1	30	27	5400
3	10	3	30	70	14000
4	10	7	30	74	14800
5	10	7	10	16.3	3620
6	10	7	70	oligomer	-

* Polymerization conditions: Reaction time = 30 minutes, Ni:MAO ratio=1:2000

^a Ni:MAO ratio=1:3000

A number of polymerization experiments were performed in which the complex prepared was used as a catalyst, MAO was used as a cocatalyst, and varying ethylene pressure and reaction temperature to study the effect on catalyst activity as shown in Table 1. The optimum condition to the best activity was found in entry 2, when used 10 μmol and the reaction temperature was set to 30 $^{\circ}\text{C}$ and the ethylene pressure was set to 3 bar.

Firstly, the temperature was held at 30 $^{\circ}\text{C}$ for 30 minutes to study the effect of the pressure effect on complex activity, 3 polymerizations were done entries 2, 3 and 4 with ethylene pressure 1, 3 and 7 bar, respectively. It was found that the activity increased by a factor of three when the pressure increased from 5400 (kg PE) (mol^{-1}Ni) h^{-1} at 1 bar to 14000 (kg PE) (mol^{-1}Ni) h^{-1} at 3 bar. The reason for this phenomenon is that increasing the ethylene pressure increases the quantity of ethylene dissolved in the solvent (ethylene concentration $[\text{M}]$) and the speed of ethylene insertion¹¹. The propagation rate (R_p) increases as the concentration of monomer increases, as shown in the equation below.

$$R_p = k[\text{M}][\text{C}]$$

where k is the propagation constant, $[\text{M}]$ the concentration of ethylene monomer and $[\text{C}]$ the concentration of the active centre.

However, when the ethylene pressure was increased to 7 bar, the activity increased from 14000 to 14800 (kg PE) (mol^{-1}Ni) h^{-1} , this increase considered to be very low comparing to the pressure increased. The same phenomena was reported before by Brookhart¹¹, where the optimum ethylene pressure was around 27.58 bar (400 psig) for three of their produced

complexes, and when the pressure increased or decreased the activity decreased again. The reason is that chain walking occurs in the cationic alkyl complex and the complex lifetime is decreased as the ethylene pressure is increased.³² The rate of insertion (chain growth) will either:

- be independent of ethylene pressure if the resting state is predominantly the alkyl-olefin complex, or
- increase with ethylene pressure if a significant fraction of the catalyst rests as the cationic alkyl complex¹¹.

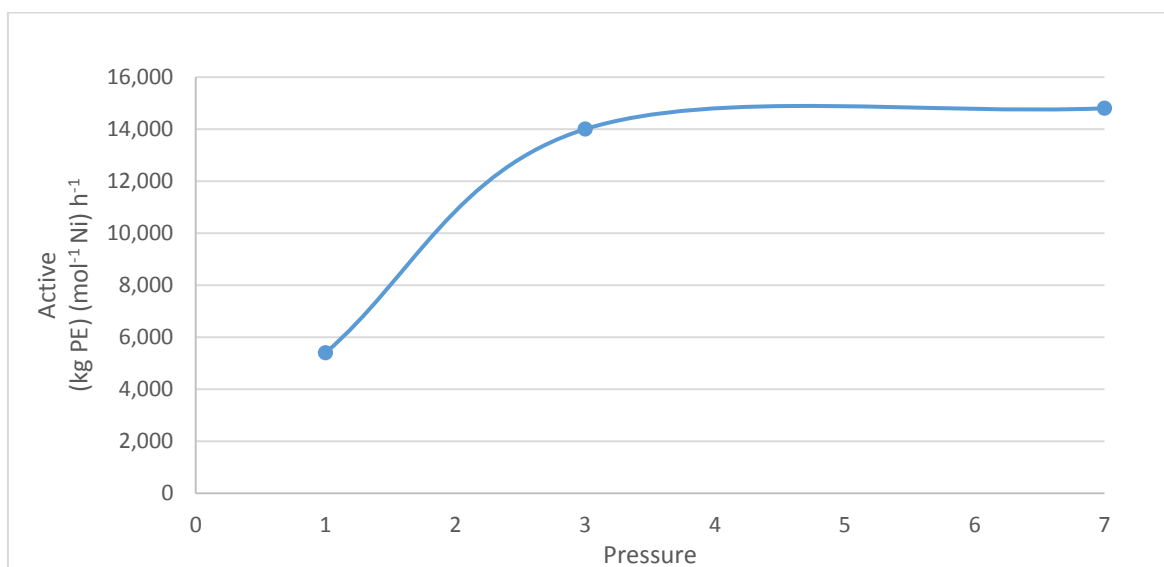


Figure 12: Active between entry (2,3,4)

The effect of temperature variation was also studied using the prepared complexes. A series of polymerizations were run in which the reaction pressure was held at 7 bar for 30 minutes, while the reaction temperature was varied, at 10, 30 and 70 °C. Table 1 summarizes the result of the effect of the reaction temperature entries 4, 5 and 6. The effect of increasing the polymerization temperature was a clear increase in catalytic activity up to the optimal temperature of 30 °C, beyond which catalytic activity decreased. when the polymerization temperature was raised from 10 to 30 °C, the catalytic activity of the catalyst jumped from 3620 to 14300 kg PE mol⁻¹ Ni h⁻¹ (entries 5 and 4), then when the temperature was increased further to 70 °C, a trace of oligomer was produced see Figure 13. This decrease must be due to an increased catalyst deactivation rate, as is known for most olefin polymerization catalysts. A reduction in the solubility of ethylene as the temperature increased may also have played some role¹¹.

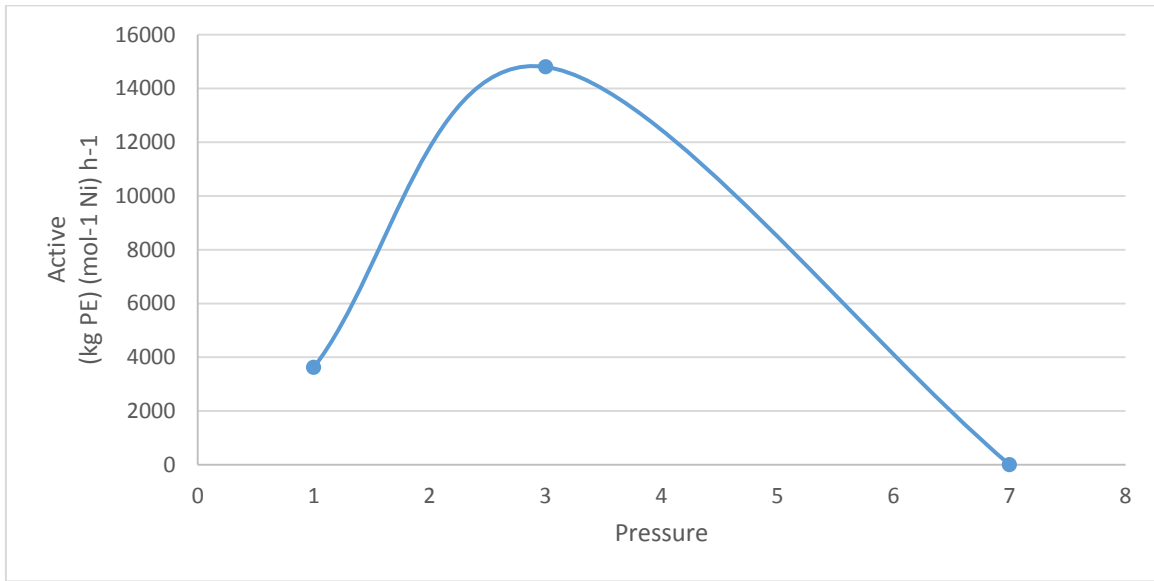


Figure 13: Active between entry (2,3,6)

5. Conclusion

To conclude, the nickel complex was synthesis and gave a nice size red-brown crystals. Then, it was used to polymerize ethylene. The complex was active and produced polyethylene, however, the activity varied from very low activity and produced a trace of oligomers to highly active to give more 70 g after 30 minutes of polymerization. The activity depends on the condition used for polymerization. For example, the optimum temperature was found to be 30 °C, and the optimum pressure was found to be 3 bar.

More work should have been done regarding the characterization of the complex and produced polyethylene, however, the lack of equipment and time forced us to write this report with current results.

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