CHAPTER THREE

Polymerization of Ethylene Using Chromium(III) and Chromium(III)-Iron(III) Mixed-metal Acetate As Catalysts

3.1 INTRODUCTION

The first PE was produced in laboratories in Imperial Chemical Industries Ltd. (ICI), England. In the early stage, PE was produced by binding ethylene molecules together in a chain from ethylene gas and using traces of oxygen as catalysts. The reaction was subjected to 1400 atm of pressure at the temperature of 170^{o}C (Billmeyer, 1984; Martin, 2007).

PE was also produced via free-radical polymerization at high pressure between 1000 – 3000 atm and temperature up to 250^{o}C. In the mechanism of radical polymerization, trace oxygen may be used to initiate the process. Besides that, peroxides, hydroperoxides and azo-compounds have also been used as initiators. Other than that, the polymerization can be performed in solution of benzene or chlorobenzene at temperature of about 200^{o}C and pressure of 1000 atm. The products were high-pressure PE and branched (Moore, 1963).

In 1953, at the Max-Plank-Institute for Coal Research in Mulheim, Karl Ziegler and co-workers made an important discovery. The ethylene monomer could be polymerized in solution at common temperature and pressure to give a high-molecular-weight linear polymer by using catalysts. The catalysts system involved aluminium and other metal alkyls in combination with metallic halides (Moore, 1963). A high-crystalline PE was produced containing a linear structure with practically no branching polymer chain (Martin, 2007).

3.1.1 Percentage of crystallinity

Blaine reported that an understanding of the degree of crystallinity is important as the crystallinity affects the physical properties such as storage modulus, permeability, density and melting temperature (Blaine, n. d.). Therefore, measuring the percentage of crystallinity is important to determine the degree of crystallinity. In line of that, DSC anaylisis is one of the method to measure the degree of crystallinity. The enthalpy of fusion obtained from the area under the endotherm peak was used to calculate the percentage of crystallinity. The percentage of crystallinity is defined as:

$$\text{Percentage of Crystallinity} = (\Delta Hm / \Delta Hm°)\ 100\%$$

Where, ΔHm is the heat of melting point and ΔHmo = 293.0 J g-1 and is the melting enthalpy of pure crystalline HDPE at equilibrium melting point (Kong & Hay, 2002; Zaydouri & Grivet, 2009).

3.1.2 Kinetic study

Natta and co-workers have proposed a kinetic scheme for polymerization involving three steps, namely initiation, propagation and chain termination (Boor, 1979). Whereas, Huang and Rempel specifically proposed the kinetic model due to mechanism in propagation (Huang & Rempel, 1995).

The consumption of monomer is proportionally related to the formation of PE hence the usage of monomer gas plays an important role to determine the rate of polymerization. The polymerization rate in this work was monitored by observing the rate of pressure drop. The rate law equation was determined by applying the ideal gas law, where the pressure and volume of monomer gas are directly proportional to the number of moles. In a closed system, the pressure is proportionally to the molar concentration of monomer, C.

$$P = (n/V)RT = CRT$$

R is the gas constant (0.0820 L atm K^{-1} mol^{-1}). The rate of decrease of monomer concentration is given by:

$$\frac{-dC}{dt} = kC$$

From the ideal gas law, P = CRT;

$$\frac{dP}{dt} = \frac{dC}{dt}(RT)$$

$$\frac{dP}{dt} = -kC\,(RT)$$

$$\frac{dP}{dt} = -kP$$

So

$$\frac{dP}{P} = -k\,dt$$

Where k is the overall rate constant for the polymerization reaction and P is the monomer pressure. For the first order reaction, plot of ℓn P versus time should give a straight line. Integration against the equation gives:

$$\ell n\, P = -kt + c$$

3.2 EXPERIMENTAL

The polymerization of ethylene was performed using the gasline as proposed by earlier researchers (Aishah, 1995; Ooi, 1996; Tan, 2007; Beatrice, 2009; Wong, 2010). Some provisions have been carried out to ensure that the polymerization process worked efficiently.

3.2.1 Experimental setup

The polymerization process involves the usage of catalysts and cocatalysts. Therefore, without the presence of cocatalyst, the catalyst will not show any catalytic activity. As the cocatalyst is sensitive towards air and moisture, extreme cautions was needed to avoid this condition from affecting the result. As a precaution, dry box (**Figure 3.1**) with nitrogen gas atmosphere was used to perform the preparation of the reactor flask.

All glasswares, syringes and needles were soaked in a solution of KOH in isopropyl alcohol (15%, W:V), 15 minutes in ultrasonic bath to remove any impurities and lastly washed thoroughly with distilled water. The apparatus were dried in oven at 120^{o}C for 24 hours before being use in the polymerization process.

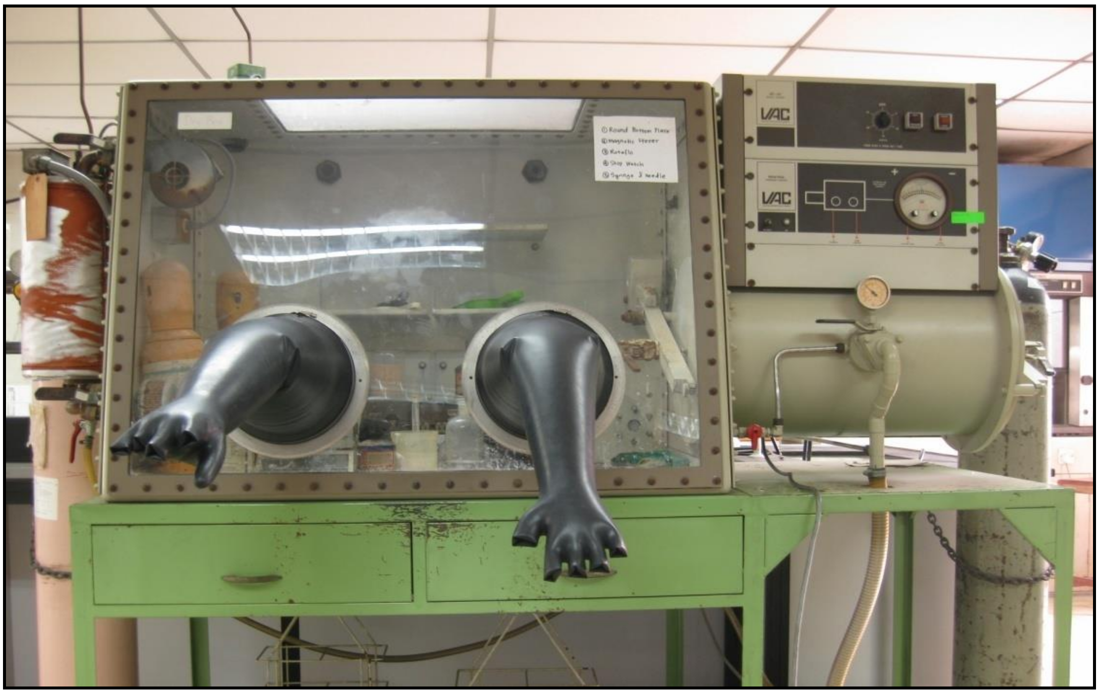

Figure 3.1: Dry box

Toluene from MERCK (A.R. grade, >99%) was purified by distillation over sodium metal under nitrogen atmosphere. The nitrogen gas was bubbled through toluene along the purification process. Pure toluene was kept dry in a stoppered bottle containing activated 3 Ǻ molecular sieves and stored in the dry box. In the gasline system, the monomer, high purity ethylene gas (99.9%) from Malaysian Oxygen Ltd. Company was passed through a column filled with activated 3 Ǻ molecular sieve and drying agent (KOH and NaOH) to avoid any moisture.

3.2.2 Constant volume setup

Constant volume is a space of gasline setup that is used for polymerization process. The constant volume will be used to measure the volume of monomer gas in every polymerization process. By measuring the volume of reactor flask and the volume of reservoir flask, the constant volume of gasline setup can be determined. **Figure 3.2** shows the scheme of gasline.

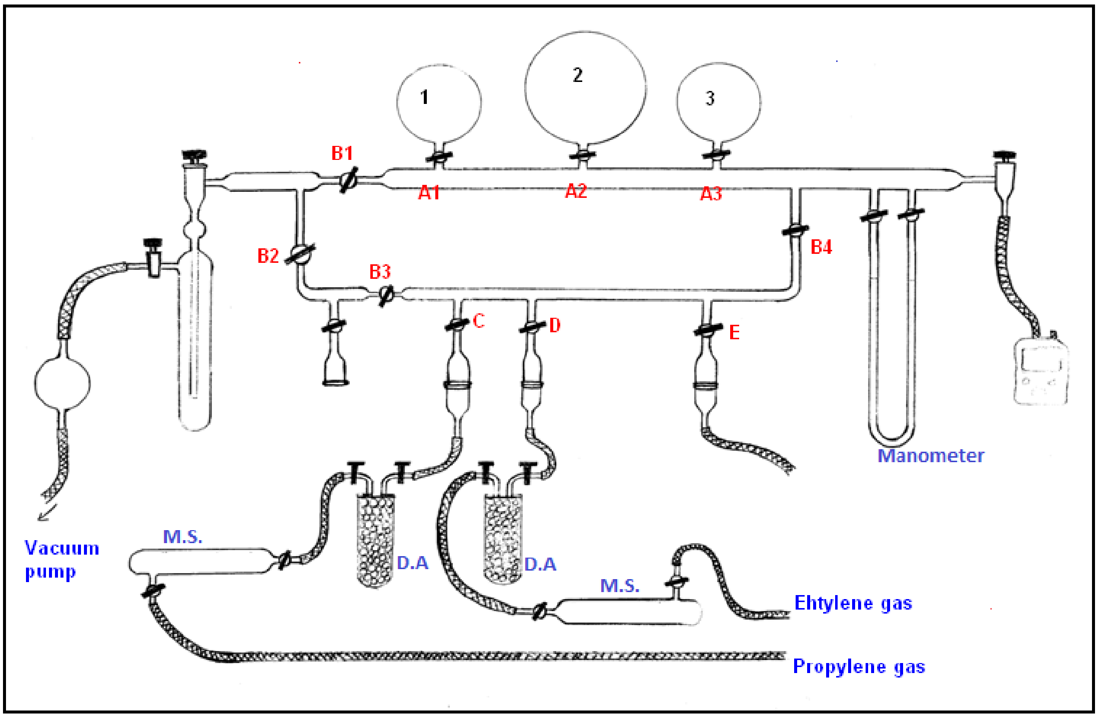

Figure 3.2: Scheme of gasline

The volume of flask was initially determined before reactor flask was joined up to the gasline system. The flask was filled up with water and the water was measured using measuring cylinder. While, the volume of gasline setup was determined by applying Ideal Gas Law, PV=nRT.

The gasline system was readily degassed for 15 minutes, before tap B1 and B3 were closed. After that, tap A1 was opened to allow reservoir flask 1 to be filled up with air through tap E. At the same time, one of the manometer taps was opened to measure the pressure in the gasline. Initial pressure, P_1 was noted after the manometer scale was stable. Then, tap A1 was closed and the gasline system was degassed over again. Tap A1 was opened and the air in reservoir flask 1 was let in to fill up in the gasline. Eventually, the final pressure P_2 recorded. The same procedure was repeated for reservoir flasks 2 and 3.

For calculation, by assuming $P_1V_1=P_2V_2$ at constant temperature and $V_2=V_1+V_D$, where V_1 is volume of flask and V_D is "dead volume" of the gasline system.

$$P_1V_1=P_2V_2$$

$$P_1V_1= P_2 (V_1+V_D)$$

So $$V_D= (P_1V_1/P_2)-V_1$$

Table 3.1: Determination of dead volume

Reservoir flask	**Volume of flask, V_1 (ml)**	**Initial pressure, P_1 (cmHg)**	**Final pressure, P_2 (cmHg)**	**Dead volume, V_D (ml)**
1	1104	75.7	51.9	506
2	4257	75.7	67.6	510
3	1094	75.7	51.7	508

Average V_D = 508 ml

Based on initial pressure, P_1 (atmosphere pressure) value, the calculated average dead volume, V_D is 508 ml. Total volume occupied by monomer gas in polymerization process was calculated by combining of the average dead volume, the volume of reservoir flask 1 and 3 (commonly used = 2198 ml), the volume of reactor flask (300 ml) minus the volume of reactor flask filled with solvent (100 ml) to give the constant volume (2198 ml + 508 ml + (300-100) ml = 2906 ml).

3.2.3 Polymerization of ethylene

Some precautions were taken since cocatalyst will react readily with oxygen and water. The preparation of reactor flask was performed under nitrogen atmosphere in a dry box (**Figure 3.1**) and the gasline system had been degassed for at least one hour before it was ready to use.

The preparation of reactor flask started with a clean, dry, 250 ml round bottom flask and a Teflon-coated magnetic stirrer bar readily loaded in the flask with 0.02 g of catalyst. Under nitrogen atmosphere, toluene (solvent) and cocatalysts were placed into the flask by using a clean, dry graduated syringe. Cocatalyst used was diethylaluminium chloride, $AlEt_2Cl$ with a concentration of 0.16 M. The volumes of solvent and cocatalyst used depend to the Al/Cr molar ratio. Total volume of reaction mixture (solvent and cocatalysts) was kept at 100 ml to obtain reproducible results. After that, the reactor flask was connected to a stopcock then, joined to gasline through tap E (refer to **Figure 3.2**).

The reactor flask which had been connected to the the gasline was first degassed into vacuum to remove the nitrogen gas. When tap E was opened, the pale-yellow solution (reaction mixture) will start to bubble. After the entire gasline system was degassed, the monomer gas was introduced into the gasline by filling reservoir flasks 1 and 3 through tap C. The monomer was first treated to remove any trace of moisture by allowing it through molecular sieves (M.S) and drying agent (D.A). The pressure of monomer gas registered by manometer was recorded. At this stage, the monomer gas had filled up the gasline system from tap B1 to tap B3 as taps C, D, E and A2 were closed.

The polymerization process began as soon as the monomer was introduced into the reactor flask from tap E. The polymerization process was monitored by observing the rate of pressure drop (cmHg). Amount of pressure drop over time was recorded during the polymerization period. The polymerization process was carried out for one hour, at room temperature and at fixed stirring speed.

The polymerization process was stopped when tap E was closed and the reactor flask removed from the gasline. The reaction mixture that contained PE was poured into a solution of 400 ml methanol acidified with 10 ml of concentrated HCl and stirred for one hour to allow precipitation of the polymer. PE formed was filtered, washed several times with methanol and left to dry in vacuum oven for 24 hours. The PE was collected, weighed and the yield was recorded.

Based on the rate of pressure drop, the kinetic data obtained were used to determine the catalytic activity. Amount of monomer consumed in the polymerization process was calculated based on the pressure drop of the monomer gas by using the ideal gas law, $\Delta n = \Delta P(V/RT)$ where Δn is the number of moles of monomer gas. While, ΔP is pressure drop, $V = 2906$ ml is constant volume that had been determined (in Section 3.2.2), R is the Universal gas constant (0.0821 L atm K^{-1} mol^{-1}) and T is the temperature of reactor system in Kelvin.

Pressure readings was observed as soon as the ethylene monomer started to flow into the reactor flask. The reaction mixture changed from clear orange solution to cloudy-orange solution indicating the formation of PE. The solvent became more viscous as the PE was forming aggressively. At the end of the polymerization, the viscous-cloudy-orange solution was poured into a solution of methanol-HCl mixture. The mixture was stirred for 2 hours while a white precipitate started to form. After filtration and thorough washing with methanol, the PE produced was dried in a vacuum oven for 24 hours and the weight was recorded.

Table 3.2 shows the kinetic data for the polymerization of ethylene using **CI[1]** with Al/Cr molar ratio of 26.2. Third column of the table represents the pressure drop calculated from the pressure reading (second column). The actual pressure drop was determined upon standardization by running a control polymerization reaction without using any catalysts and cocatalysts in the solvent system. The polymerization process was performed at 30°C for 60 minutes. The catalytic activity of catalyst was calculated based on the formation of PE and has been expressed in gPE/gCr/hr/atm unit (the calculation in **Table 3.2** was carried out using Microsoft Excel 2012). The calculation for maximum initial activity as shown in **Appendix**.

Table 3.2: Kinetic data for the polymerization of ethylene using **CI[1]** and Al/Cr molar ratio of 26.2 at 30°C

Time / min.	**Pressure reading / cmHg**	**Pressure drop* / cmHg**	**Pressure drop / cmHg (control run)**	**Pressure drop / cmHg (actual drop)**	**Catalytic activity (gPE/gCr/hr/atm)**
0.00	80.80	0.00	0.00	0.00	0.0000
0.50	77.50	6.60	4.00	2.60	2931.96
1.00	76.90	1.20	0.60	0.60	338.30
1.50	76.40	1.00	0.20	0.80	300.71
2.00	76.00	0.80	0.20	0.60	169.15
2.50	75.70	0.60	0.20	0.40	90.21
3.00	75.35	0.70	0.20	0.50	93.97
3.50	75.00	0.70	0.20	0.50	80.55
4.00	74.60	0.80	0.10	0.70	98.67
4.50	74.25	0.70	0.10	0.60	75.18
5.00	73.90	0.70	0.00	0.70	78.94
6.00	73.10	1.60	0.00	1.60	150.36
7.00	72.35	1.50	0.00	1.50	120.82
8.00	71.70	1.30	0.00	1.30	91.62
9.00	71.05	1.30	0.00	1.30	81.44
10.00	70.40	1.30	0.00	1.30	73.30
12.00	69.85	1.10	0.00	1.10	51.69
14.00	68.50	2.70	0.00	2.70	108.74
16.00	67.70	1.60	0.00	1.60	56.38
18.00	67.00	1.40	0.00	1.40	43.85
20.00	66.40	1.20	0.00	1.20	33.83
25.00	65.20	2.40	0.00	2.40	54.13
30.00	64.20	2.00	0.00	2.00	37.59
35.00	63.45	1.50	0.00	1.50	24.16
40.00	62.80	1.30	0.00	1.30	18.32
45.00	62.25	1.10	0.00	1.10	13.78
50.00	61.80	0.90	0.00	0.90	10.15
60.00	60.95	1.70	0.00	1.70	15.98

*Pressure drop obtains from pressure reading

3.2.4 Characterization of polymer

Characterization of the polymer was carried out by spectroscopic method and thermal analysis study. IR spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to describe the characteristic of the polymers.

a) IR spectroscopy

Vibrational spectra of polymer were analysed using attenuated total reflection infrared (ATR-IR) spectroscopy. The spectrum was recorded in the range of 4000 – 600 cm^{-1} using Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer.

b) Thermal gravimetric analysis (TGA)

For thermogravimetric analysis (TGA), 10 mg of PE was placed on a TGA pan. Perkin Elmer Pyris Diamond TG/DTA instrument was used to analyse the PE sample under nitrogen atmosphere with flow rate of 20 ml/min, a scan rate of 20^{o}C/min and a temperature range of 50 – 900^{o}C.

c) Differential scanning calorimetric (DSC)

Differential scanning calorimetric (DSC) was recorded on Perkin Elmer DSC 6 under nitrogen gas atmosphere. The flow rate of nitrogen gas was 10 ml/min and scan rate was 10^{o}C/min. About 2 mg of PE was placed on an aluminum crucible and transferred to the DSC instrument. The sample was heated from 50 – 200°C and hold for 10 minutes at 200°C before cooled from 200 – 50°C. After that, the sample was reheated from 50 – 200°C under the same condition as in the first heating.

3.3 RESULTS AND DISCUSSION

The complexes prepared in **Chapter Two** were used as catalysts in the polymerization of ethylene. Each complex was used as catalyst in a different set of polymerization to find out the effect of metal complexes towards polymerization. Other than that, the polymerization was also carried out by varying Al/Cr molar ratio to find significant Al/Cr molar ratio with highest catalytic activity and highest polymer yield. The polymerization had also been performed under a variation of temperatures. **Figure 3.3** shows the PE obtained from the polymerization process.

Figure 3.3: Polyethylene obtained from the polymerization using **CI[1]** and Al/Cr molar ratio of 26.2 at 30°C

Boor (979) discovered several important factors that influenced Ziegler-Natta catalyst kinetics and stereochemical behaviour. The choice of metal and the nature of the ligands play an important role in selection of cocatalysts. The crystal structure, and the electron valence will also affect the catalytic activity. Furthermore, the way the components were brought together and used in polymerizations such as absolute and relative concentrations, aging, temperature and time also have an effect. Thus, the polymerization of ethylene was carried out by varying cocatalyst/catalysts ratio (Al/Cr molar ratio), changing the nature of ligands (by changing with benzoate instead of acetate ligand) and varying the temperature of polymerization system.

3.3.1 Polymerization of ethylene

The preparation of reactor flask was performed in the dry box where the complex, cocatalyst and solvent were added together into a reaction flask. Aliphatic and aromatic hydrocarbons were commonly used as solvent for the polymerization. However, the usage of toluene as solvent contributed to higher rates of polymerization as had been reported (Boor, 1979). Meanwhile, the catalysts (complex) were ground to increase their catalytic activity as grinding increases the surface area for reaction to occur (Kissin, 1985).

The mixture in the reactor flask was left to age for 15 minutes before the monomer gas was being introduced. Previous studies found that 15 minutes of aging time lead to a maximum activity but prolonged aging time leads to drop in catalytic activity (Aishah, 1995). The solvent colour changed from colourless to pale yellow as soon as the cocatalysts were added and then turned into orange after aging for 15 minutes. The change of colour is due to the reduction of Cr^{3+} to Cr^{2+}, which shows that the catalyst complex is active. Several studies have confirmed that the Cr^{2+} is the active state in the polymerization of ethylene (Gan, *et al.*, 1987; Soga, *et al.*, 1985a).

Soga, *et al.*(1985a) found that $Cr(C_{17}H_{35}COO)_3$ in toluene did not polymerized neither ethylene nor propylene in the absence of alkylaluminum compunds. Moreover, the catalytic activity of the polymerization of ethylene using $AlEt_2Cl$ as cocatalyst is much higher than that obtained by using $AlEt_3$ and $Al_2Et_3Cl_3$ as cocatlysts, therefore $AlEt_2Cl$ was used as cocatalysts for the study (Soga, *et al.*, 1985a; Soga, *et al.*, 1985b). This might be due to the over reduction of Cr species from active Cr^{2+} to inactive Cr^{1+} or Cr^0 by $AlEt_3$ and $Al_2Et_3Cl_3$ (Gan, *et al.*, 1984).

The formation of PE started once the introduction of ethylene monomer into the reactor flask as the cocatalyst and catalyst reacted readily in the reactor flask (Gan, *et al.*, 1987). **Figure 3.4** shows the pressure drop that represented the amount of monomer gas used in the polymerization process. The accumulative yield for the formation of PE is shown in **Figure 3.5**. As the pressure drop increases the formation of PE increases. Chirkov *et al.* have proposed that the rate of polymerization is directly proportional to the monomer concentration (Keii, 1972).

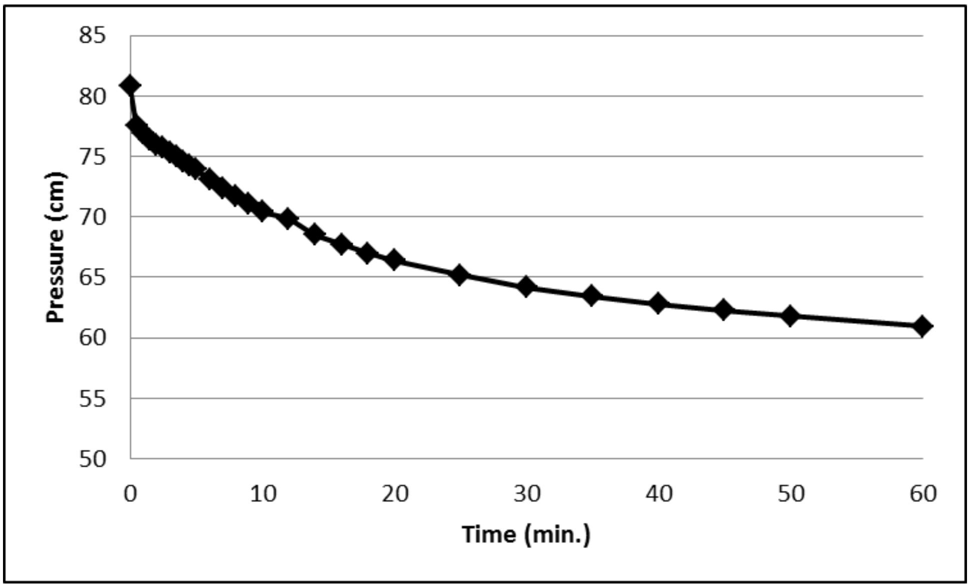

Figure 3.4: Plot of drop in preassure versus time for the polymerization of ethylene using **CI[1]** and Al/Cr molar ratio of 26.2 at 30^{o}C

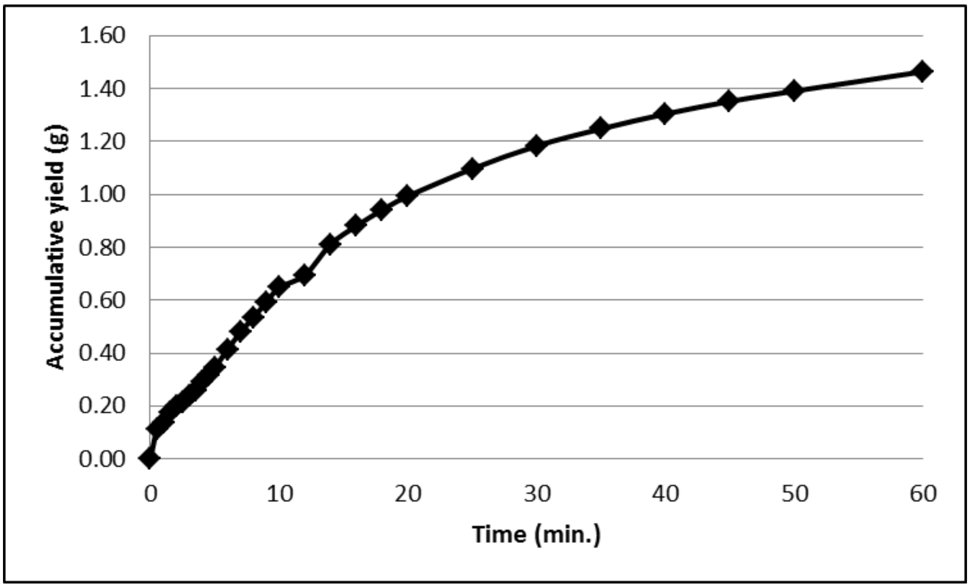

Figure 3.5: Plot of accumulative yield versus time for the polymerization of ethylene using **CI[1]** and Al/Cr molar ratio of 26.2 at 30^{o}C

PE was rapidly formed in the first 20 minutes of the polymerization and then slowed down steadily until the end of polymerization. The rate of PE formation slowed down because the number of active sites decrease and the increment of solution viscosity. Furthermore, the formation of PE decreased because the monomer gas could not reach the active site as it was encapsulated by PE. An aggressive formation in the early period of the polymerization brought to the encapsulation of PE. The precipitation of PE in a solvent system leads to the non-uniform of stirring spin that causes the decrease in rate of polymerization (Gan, *et al.*, 2000). Keii (1972) has reported that the rate of polymerization is proportional to the stirring speed due to the mass transfer effect.

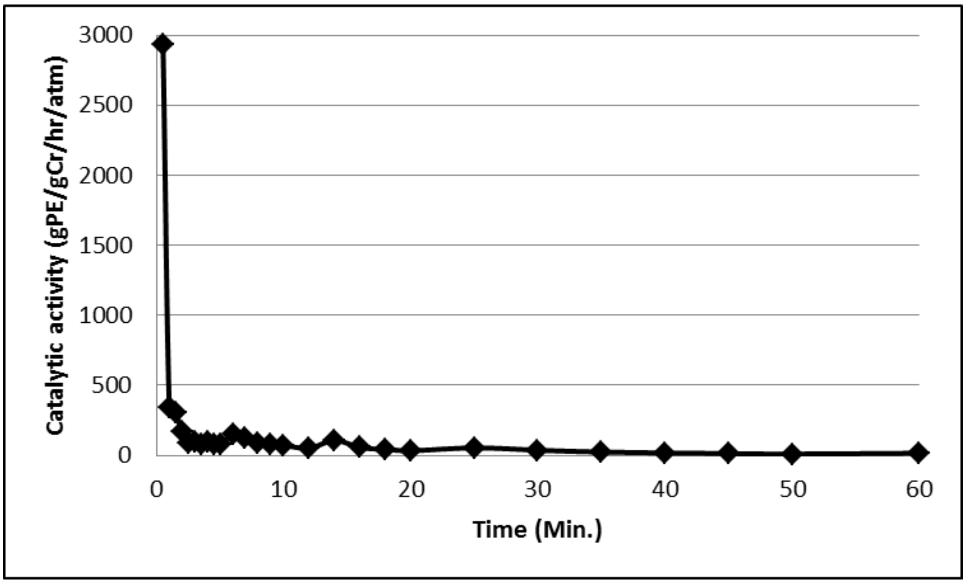

Figure 3.6: Kinetic curve for the polymerization of ethylene using **CI[1]**, Al/Cr molar ratio 26.2 at 30°C

The kinetic curve for the polymerization of ethylene using **CI[1]** at 30^{o}C with Al/Cr molar ratio of 26.2 is shown in **Figure 3.6**. Higher catalytic activity was recorded in the early 20 minutes before decreasing steadily as the polymerization process was prolonged. The catalytic activity was closely related to the pressure drop of monomers and the formation of PE. The catalytic activity was increased when the rate of the PE formation was increased. The kinetic curve shows that the highest catalytic activity is observed in the early period due to the breaking of the catalyst particle which exposes new surfaces and forms new centres for polymerization process. However, the catalytic activity decreased with time because the active centres may have become unstable due to some structural changes (Gan, *et al.*, 1987). Moreover, the centres are encapsulated with the polymer, hence the monomer has difficulty to diffuse from the liquid through the polymer to the centres (Boor, 1979).

The kinetic curve for the polymerization of ethylene is a decay type as reported by Keii (1972) where the rate curve reaches its maximum and subsequently declines as observed in **Figure 3.6**. Boor (1979) has proposed that the decline in polymerization rate is caused by the decrease in the number of active centres, reducing the activity of individual centres due to structural changes and the shortage of monomer in the vicinity of the centre.

3.3.2 Effect of varying Al/Cr molar ratio

Series of ethylene polymerizations were carried out by varying Al/Cr molar ratio to investigate the Al/Cr molar ratio that gives the highest catalytic activity. All complexes are used in the polymerization except **CI[4]** as it did not show any catalytic activity in the polymerization of ethylene.

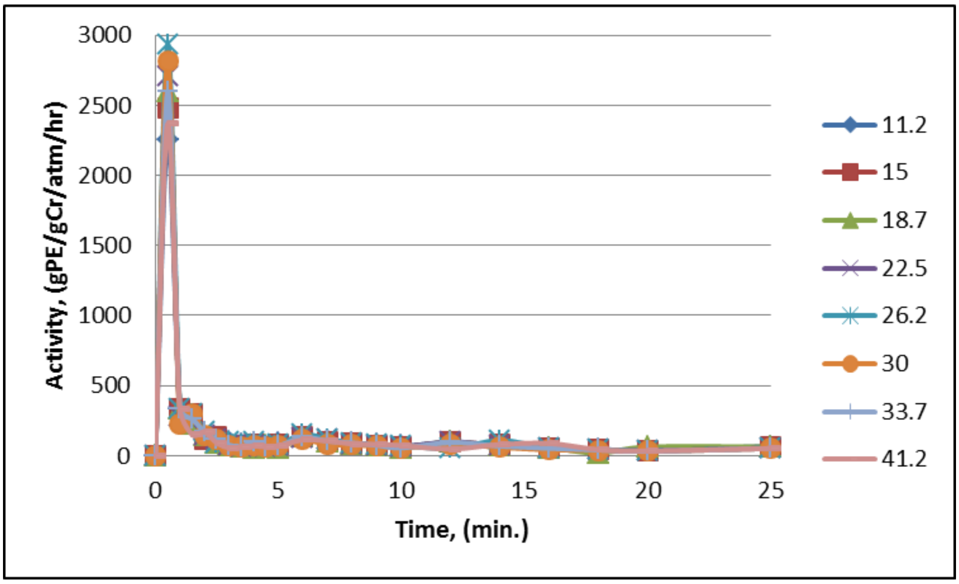

Figure 3.7: Kinetic curve for the polymerization of ethylene using **CI[1]** at 30^{o}C with different Al/Cr molar ratios

Figure 3.7 shows the kinetic curves for polymerizations of ethylene using **CI[1]** performed at 30^{o}C using variable of the Al/Cr molar ratios. The kinetic curve is plotted for 25 minutes duration to show a significant difference in the polymerization as the critical period for polymerization occurrs in the early stage of the process. The kinetic curve for other complexes are attached in the Appendix. All the polymerization series were performed under similar condition where the temperature of the reactor was 30^{o}C and 1 atm pressure.

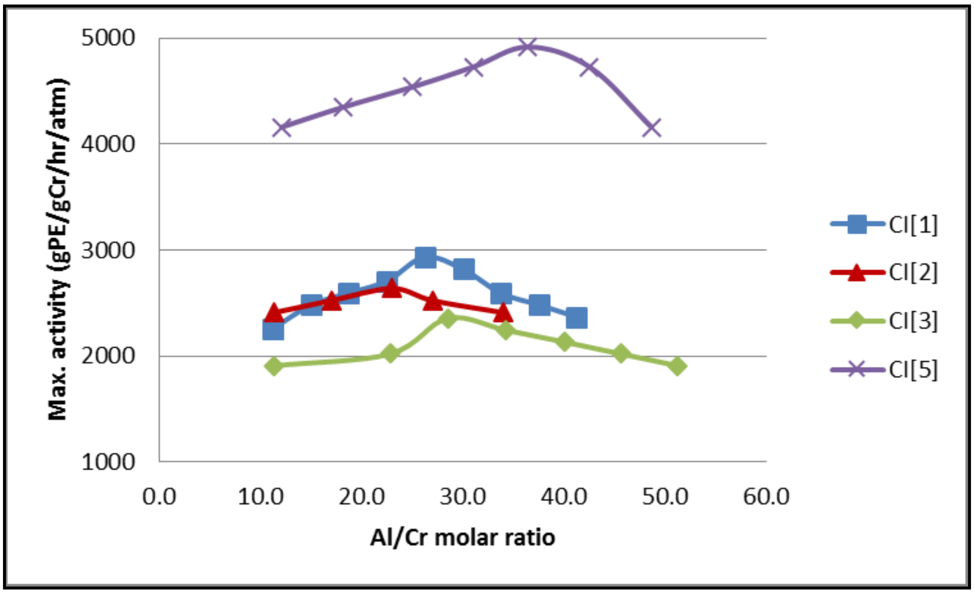

Figure 3.8: Plot of maximum initial activity versus Al/Cr molar ratio for the polymerization of ethylene

A variation of the Al/Cr molar ratios in the polymerization of ethylene using **CI[1]** was investigated from 11.2 to 41.2. The catalytic activity increased as the Al/Cr molar ratio was increased from 11.2 to 26.2 and decreased with further increase in the Al/Cr molar ratio. **Figure 3.8** shows the plot of maximum initial activity versus Al/Cr molar ratio for **CI[1]**, **CI[2]**, **CI[3]** and **CI[5]**.

The pattern of the plot of maximum initial activity versus Al/Cr molar ratio was approximately for **CI[2]**, **CI[3]** and **CI[5]**. The maximum initial activity increased as the Al/Cr molar ratio was increased to optimum ratio. However, the maximum initial activity dropped when the Al/Cr molar ratio was above the optimum ratio. The optimum Al/Cr molar ratio that gave the highest maximum initial activity for **CI[2]**, **CI[3]** and **CI[5]** were 23 , 28.5 and 36.4 respectively. **Table 3.3** summarises the results for variation of the Al/Cr molar ratio towards the polymerization of ethylene.

Table 3.3: Optimum Al/Cr molar ratio and the maximum initial activity of the polymerization of ethylene at 30^{o}C

Catalyst	Al/Cr molar ratio	Max. initial activity (gPE/gCr/hr/atm)
CI[1]	26.2	2932
CI[2]	23.0	2637
CI[3]	28.5	2355
CI[5]	36.4	4917

The polymerization activity is highly dependent on the nature of the catalyst and the molar ratio of catalyst/cocatalyst. Natta and Pasquon (1959) found that the concentration of alkyl aluminium influences the polymerization kinetics. The maximum initial activity was low at the lower Al/Cr molar ratio because of the incomplete activation of the active centres on the catalyst by cocatalyst.

The complex catalyst containes the coordinated H_2O that is attached to the Cr ions causing more alkyl aluminium to be consumed. Some of the alkyl aluminium will react with the H_2O molecules before reducing Cr^{3+} to active Cr^{2+} (Aishah, 1995). The oxidation state of Cr in the catalyst was 2+ but Gan, *et al.*, (1984) reported that only high spin Cr^{2+} is the active catalysts while low spin Cr^{2+} is inactive. The reaction of Cr complex with $AlEt_2Cl$ at low Al/Cr molar ratio leads to a low spin Cr^{2+} while at higher Al/Cr molar ratio, an active high spin Cr^{2+} is generated.

The maximum initial activity is found to decrease with the higher consumption of the Al/Cr molar ratio. Over reduction of Cr ions to a lower oxidation state, which is inactive for the polymerization of ethylene would occur in the presence of excess alkyl aluminium. Some researchers have reported the same results where over-reduction of Ti from 4+ to its valence state 2+ was inactive for the polymerization (Keii, 1972;

Tatizawa & Quijada, 1992). McKenzie et. al suggested that reversible active centres are deactivated by adsorption of free alkyl aluminium as the concentration of alkyl aluminium is increased (McKenzie, *et al.*, 1972).

3.3.3 Effect of mixed-metal complexes

Four complexes were synthesized by varying their metal ratio (Cr/Fe). Complexes of **CI[1]**, **CI[2]**, **CI[3]** and **CI[4]** were prepared and have been characterized in **Chapter Two**. The complexes were used as catalysts for polymerization of ethylene to verify their catalytic properties. The polymerization of ethylene was performed using the different catalysts at the optimum Al/Cr molar ratio, at 30^{o}C and 1 atm pressure. The effect of the Al/Cr molar ratio towards polymerization was discussed in **Section 3.3.2**.

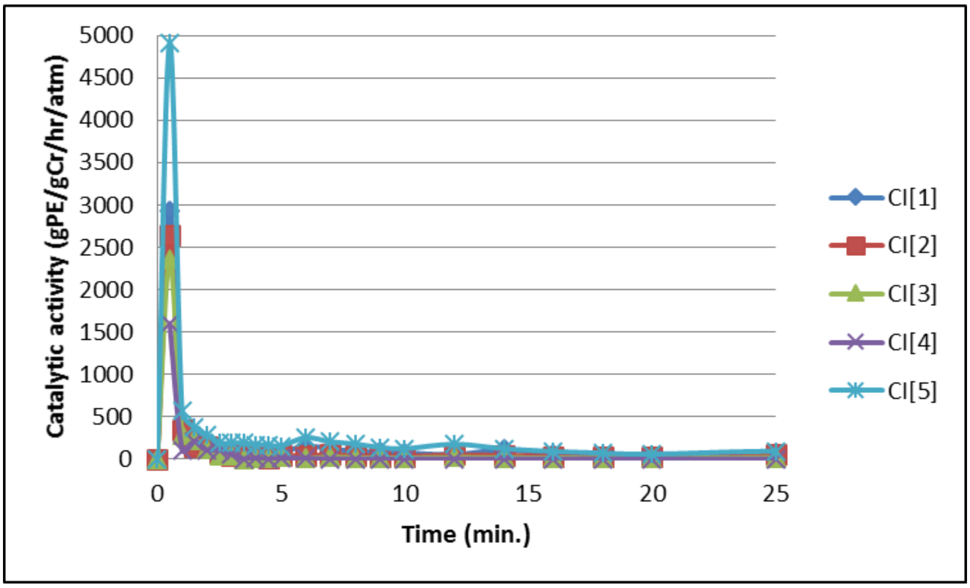

Figure 3.9: Kinetic curve for the polymerization of ethylene using different catalysts at 30^{o}C at the optimum Al/Cr molar ratio

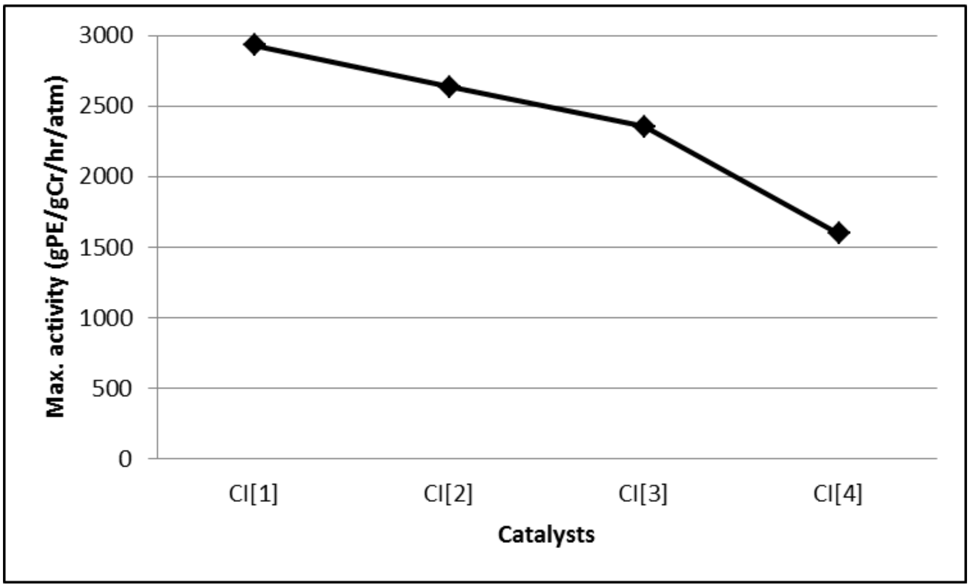

Figure 3.10: Plot of the maximum initial activity of the complexes in the polymerization of ethylene at 30°C

Polymerization of ethylene using **CI[1]**, **CI[2]**, **CI[3]** and **CI[4]** are found to exhibit significant differences in the initial catalytic activity for the first 20 minutes and these differences could be seen in **Figure 3.9**. In **Figure 3.10** the highest value of catalytic activity is demonstrated by **CI[1]**, followed by **CI[2]** and **CI[3]**. **CI[1]** contains three Cr, **CI[2]** contains two Cr and **CI[3]** has only one Cr in the complex. The results prove that Cr contributes to the catalytic properties of the catalyst complex. Meanwhile, catalyst **CI[4]** which contains only Fe does not show any significant catalytic activity in the polymerization of ethylene.

Figure 3.11 shows the accumulative yield of PE in 60 minutes of polymerization. **CI[1]** gives the highest yield of PE followed by **CI[2]** and **CI[3]**. Meanwhile, the polymerization of ethylene using **CI[4]** does not produce any PE and the formation of PE (theoretically) was stopped after 5 minutes of the process.

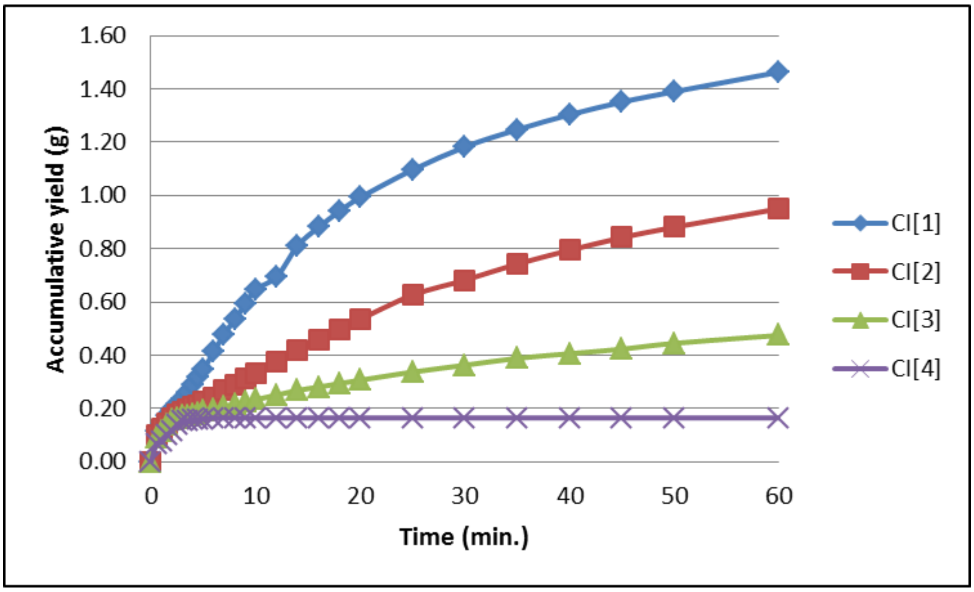

Figure 3.11: Plot of accumulative yield versus time for every complexes in the polymerization of ethylene at 30°C

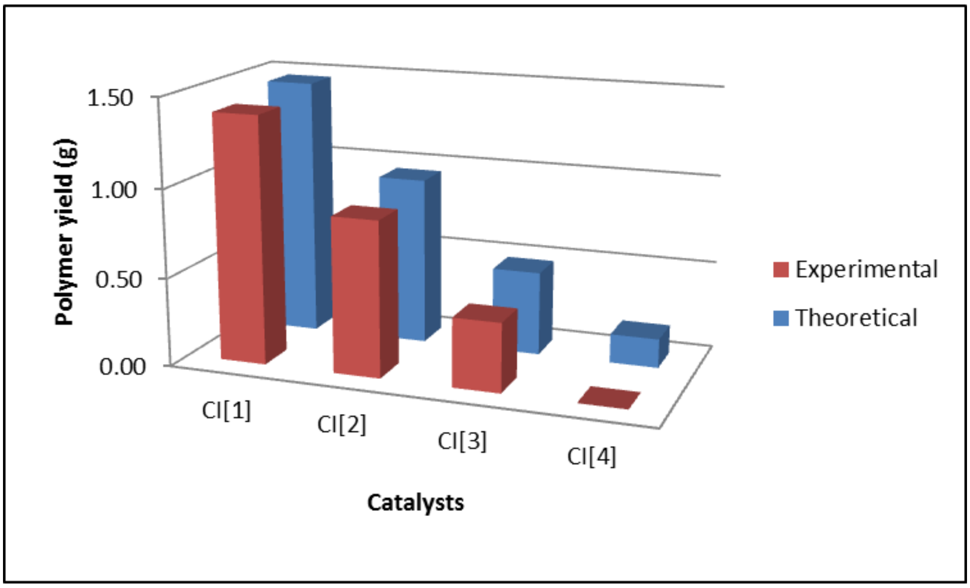

Figure 3.12: Yield of the PE

Table 3.4: Catalytic activity and the yield of PE produced by various catalysts

Catalysts	Max. initial Activity (gPE/gCr/hr/atm)	Theoretical Yield (g)	Experimental Yield (g)
CI[1]	2932	1.46	1.40
CI[2]	2637	0.95	0.88
CI[3]	2355	0.47	0.39
CI[4]	1598	0.16	0.00

Figure 3.12 shows the theoretical and the experimental yields of PE. The experimental yield is directly proportional to the theoretical yield where the experimental yield increase as the calculated yield increased. **Table 3.4** shows the relationship between Cr content in the catalyst, the value of maximum activity and the yield of PE. Higher number of Cr in the catalysts contributes to the higher catalytic activity and eventually the formation of PE also will increase. However, the Fe complex (**CI[4]**) was unsuccessful to polymerize the ethylene monomer.

3.3.4 Effect of substituent group in catalysts

The presence of electron donor in the catalyst complex was reported to affect the polymerization process and the polymer produced. The addition of electron donors to the catalyst system will change the catalytic activity or molecular weight and the stereochemical character of the polymer (Boor, 1979). Meanwhile, Alshaiban and Soares reported that the internal or external donor systems affected the stereoregularity of polypropylene. The external donor in the catalyst system reduces the deactivation term as the presence of the external donor causes the nonspecific sites to deactivate faster than the specific sites. The heterogeneous Ziegler-Natta catalyst in combination with the external donors was reported to produce a polypropylene with distinct molecular weight-averages, polydispersities, and tacticity at the same polymerization conditions. Moreover, a higher electron density leads to increase in the effectiveness of the electron donor (Alshaiban & Soares, 2012).

The kinetic curves for the polymerization of ethylene using **CI[1]** and **CI[5]** are presented in **Figure 3.7**. **CI[1]** and **CI[5]** demonstrates a same pattern in the kinetic curve, where the catalytic activity was a *decay type*. Meanwhile, **Figure 3.8** shows **CI[5]** exhibit higher catalytic activity than **CI[1]** with variation in Al/Cr molar ratio. According to Gan *et al.* (2000) the metallic centre attached to the electron withdrawing substituents reduces faster by alkyl aluminium than those attached to the electron donating substituents. Therefore, the catalytic activity increases as the number of active sites increase due to the fast reduction of Cr^{3+} to active Cr^{2+} and eventually polymerization process rapidly occurrs. **Table 3.5** summarizes the catalytic activity and the yield of PE. At optimum Al/Cr molar ratio, the maximum initial activity and the polymer yield of **CI[5]** is higher than **CI[1]**.

Table 3.5: Catalytic activity and yield of PE using **CI[1]** and **CI[5]** at 30°C

Catalysts	Max. initial Activity (gPE/gCr/hr/atm)	Theo. Yield (g)	Exp. Yield (g)
CI[1]	2932	1.46	1.40
CI[5]	4917	1.47	1.45

3.3.5 Effect of temperature

The polymerization process was carried out at the various temperature to determine the most effective temperature for the complexes to exhibit the highest catalytic activity. The polymerization was performed by using **CI[1]** and **CI[5]** at 1 atm atmosphere. Temperature of the reactor was varied at $0^{o}C$, $30^{o}C$, and $40^{o}C$.

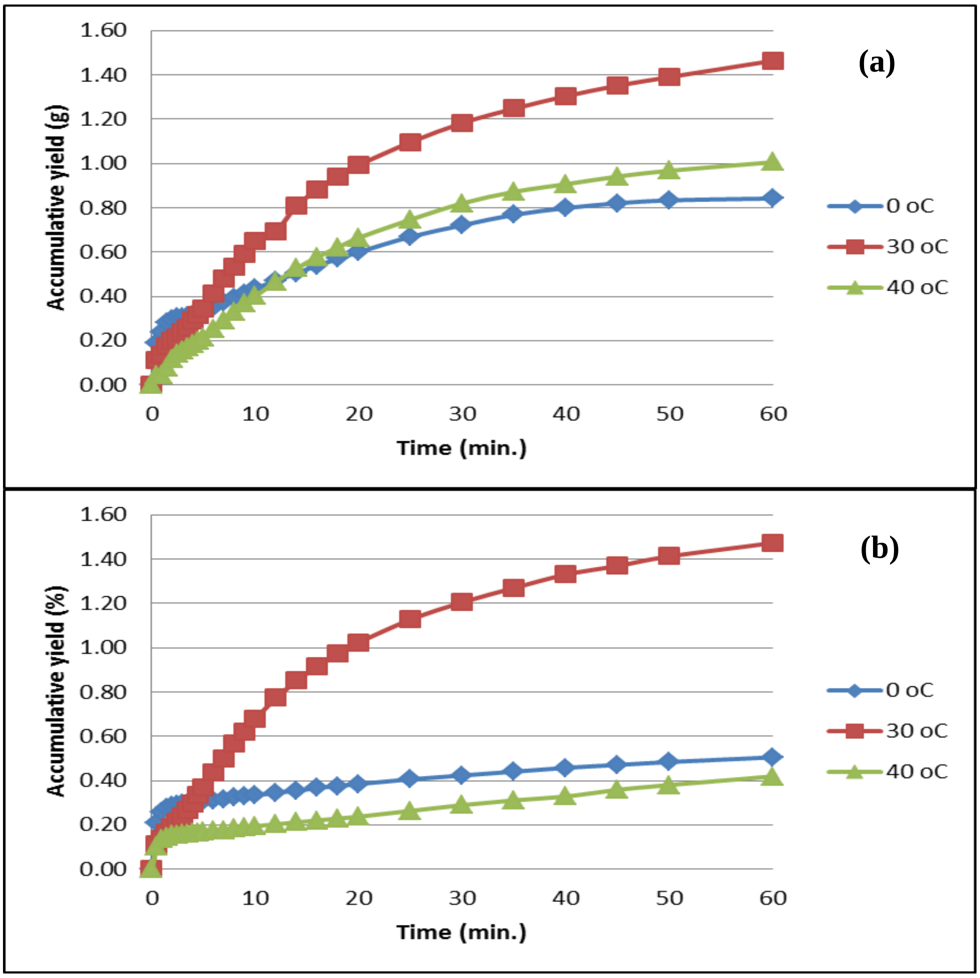

Figure 3.13: Accumulative yield for the polymerization of ethylene at different temperatures using: (a) Catalyst **CI[1]** (b) Catalyst **CI[5]**

Figure 3.13 shows the plot of accumulative yield versus time for **CI[1]** and **CI[5]** at different temperatures. In first 5 minutes of the process, the polymerization at 0°C shows the highest rate in the formation of PE. However, the formation of PE deacreases drastically especially after 10 minutes as the process proceeds 60 minutes. Temperature of 30°C is found to be the most significant condition for the polymerization of ethylene. Meanwhile, the formation of PE is low for the polymerization process performed at 40°C.

Table 3.6: Catalytic activity and yield of PE polymerized using **CI[1]** and **CI[5]** at different temperatures

Catalyst	**Temperature (°C)**	**Max. initial Activity (gPE/gCr/hr/atm)**	**Theo. Yield (g)**	**Exp. Yield (g)**
CI[1]	**0**	4962	0.84	0.81
	30	2932	1.46	1.40
	40	1128	1.01	0.99
CI[5]	**0**	9077	0.51	0.47
	30	4917	1.47	1.45
	40	4539	0.42	0.40

Table 3.6 summarises the maximum initial activity and the yield of PE for **CI[1]** and **CI[5]**. The maximum initial activity for polymerizations at 0°C was the highest but the yield was the lowest compared to 30°C and 40°C. This is due to the encapsulation of active centres by the rapid formation of PE. Soga, *et al.* (1985b) proposed that the active species became unstable with increase in the polymerization temperature. Therefore, the most suitable temperature for the polymerization of PE that gives a significant maximum initial activity and the highest yield is at 30°C.

3.3.6 Kinetic of polymerization

Plot ℓn P versus time for polymerization of ethylene using **CI[1]** is shown in **Figure 3.14**. A straight line of ℓn P versus time for the first 10 minutes indicates that the reaction is a first order reaction in the polymerization. After that, the linearity starts to deviate due to the deactivation of active centres.

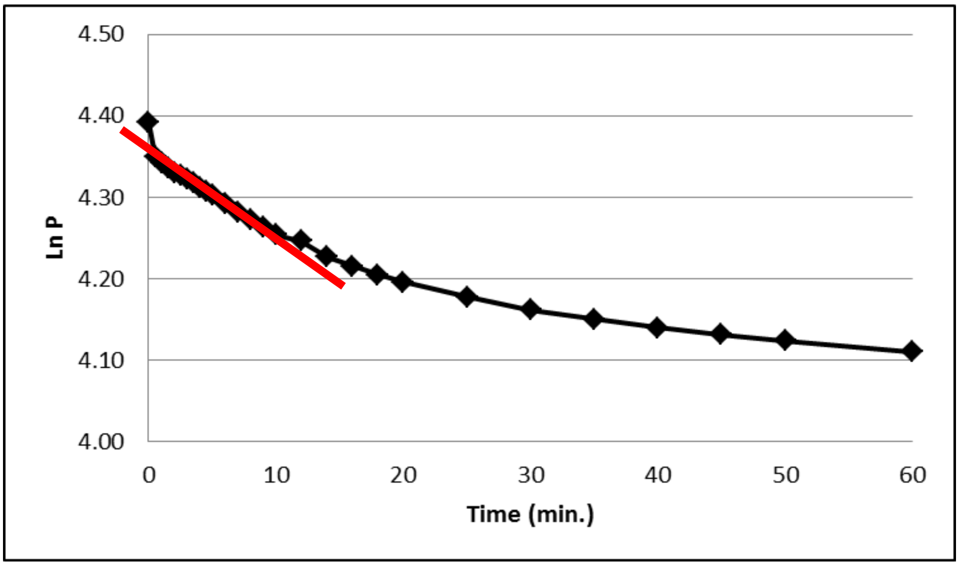

Figure 3.14: Plot of ℓn P versus time using **CI[1]**

3.3.7 Characterization of Polymer

PE is a rigid plastic because of its linear sequence and has a strong tendency to crystallise at normal temperature. One of the common PE group is the high density polyethylene (HDPE). HDPE contains a small number of molecular chains that can easily crystallise therefore the nature of HDPE is mobile and rigid amorphous phase (Galovic, *et al.*, 2012; Gan, *et al.*, 1985).

PE is categorized as one of the semi-crystalline polymers that contains two primary components which are crystalline and amorphous phases. Several factors that affect the overall crystallinity are average molecular weight, molecular weight distribution, degree of branching and/or crosslinking, presence of copolymers, concentration of additives and the thermal history of the polymer formulation (Sichina, 2000a). The most important properties of semi-crystalline polymers are the percentage of crystallinity that describes the relationship between the overall level of crystalline and the amorphous components. The percentage of crystallinity controlled the properties of semi-crystalline polymer such as brittleness, toughness, stiffness or modulus, optical clarity, creep or cold flow, barrier resistance and long term stability (Sichina, 2000b)

a) IR spectroscopy

IR spectrum were recorded using ATR-IR spectroscopy as a function of percentage of transmittance versus wave number. Interpretation of IR spectrum was carried out by referring to some literature reports (Hagemann, *et al.*, 1989; Jones & Lauer, 1979; Rojas, *et al.*, 1997; Krimm, 1956). **Figure 3.15** shows the IR spectrum of PE-**CI[1]** produced using Al/Cr molar ratio of 26.2.

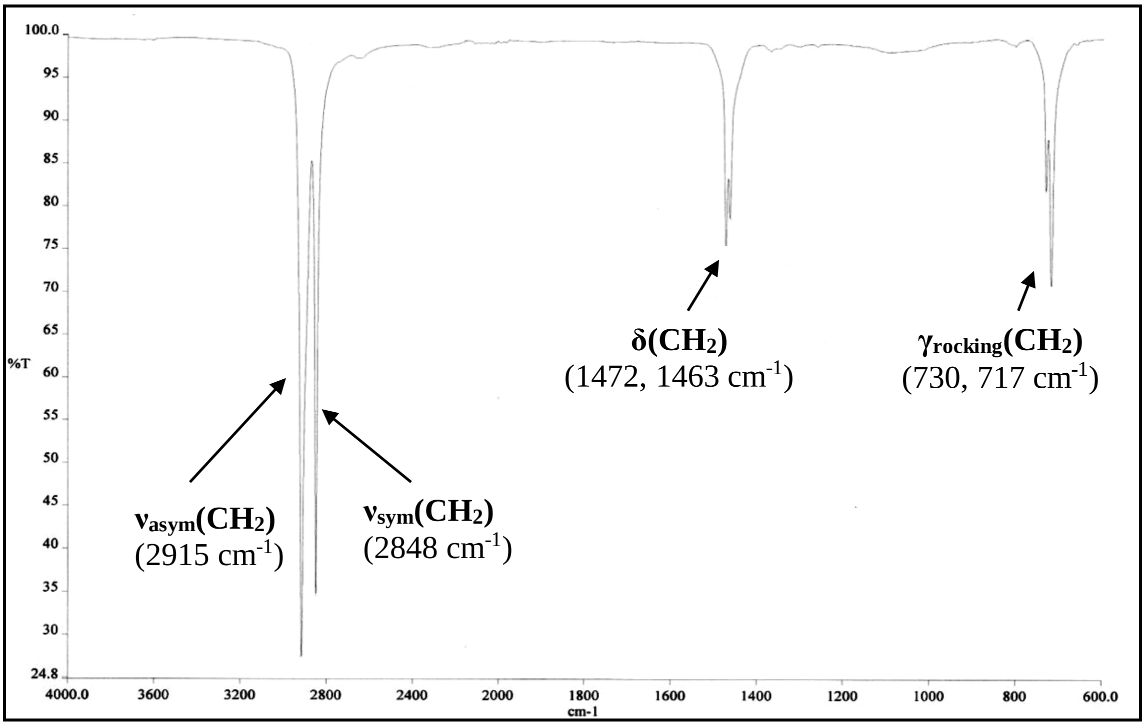

Figure 3.15: IR spectra of PE-**CI[1]**

The most intense bands are observed at 2915 cm^{-1}, 2848 cm^{-1}, 1472 cm^{-1}, 1463 cm^{-1}, 730 cm^{-1}and 717 cm^{-1} for all PE produced using **CI[1]**, **CI[2]**, **CI[3]** and **CI[5]**. **Tables 3.7** and **3.8** summarize the assignment of the PE spectra.

Table 3.7: Bands assignment for the IR spectrum of PE

Band assignment	**Group frequency, wavenumber (cm^{-1})**			
	PE-CI[1]	**PE-CI[2]**	**PE-CI[3]**	**PE-CI[5]**
$\nu_{asym}(CH_2)$	2915	2915	2915	2915
$\nu_{sym}(CH_2)$	2848	2848	2848	2848
$\delta(CH_2)$	1472, 1463	1472, 1463	1472, 1463	1472, 1463
$\gamma_{rocking}(CH_2)$	730, 717	730, 717	730, 717	730, 717

Table 3.8: Bands assignment for the PE-**CI[1]** IR spectrum at different Al/Cr molar ratios

Band assignment	**Group frequency, wavenumber (cm^{-1})**					
	11.2	**18.7**	**26.2**	**30.0**	**33.7**	**41.2**
$\nu_{asym}(CH_2)$	2915	2915	2915	2915	2915	2915
$\nu_{sym}(CH_2)$	2848	2848	2848	2848	2848	2848
$\delta(CH_2)$	1472, 1463	1472, 1463	1472, 1463	1472, 1463	1472, 1463	1472, 1463
$\gamma_{rocking}(CH_2)$	730, 718	730, 718	730, 718	730, 718	730, 718	730, 718

Two sharp bands due to asymmetric and symmetric stretching of methylene in PE appear at 2915 cm^{-1} ($\nu_{asym}(CH_2)$ and 2848 cm^{-1} $\nu_{sym}(CH_2)$ respectively. However, one set bands associated with the amorphous fraction, which is assigned to specific type of short conformational sequences are found to be absent in the 1400 – 1250 cm^{-1} region.

Three bands arise from methylene rocking, $\gamma_{rocking}(CH_2)$ should appear around ~725 cm^{-1} representing the both amorphous and crystalline fractions of PE. However, the IR spectrum shows only two sharp bands at 730 cm^{-1} and 718 cm^{-1} corresponding to the crystalline fraction. The third band for the rocking mode of amorphous fraction was hidden at ~723 cm^{-1}. This broad band is overlapped by two sharp bands of crystalline fraction.

Two sharp bands at 1472 cm^{-1} and 1463 cm^{-1} reflect the methylene scissoring mode bands, $\delta(CH_2)$. As for methylene rocking bands, $\delta(CH_2)$, three bands should appear in these region but only two bands representing the crystalline fraction are observed. The amorphous band, which is much broader, is buried at 1467 cm^{-1}.

b) Thermal gravimetric analysis (TGA)

TGA measurement providing valuable information to select materials for certain end-use applications, to predict product performance and improve product quality. The technique is particularly useful for compositional analysis of multi-component materials or blends, thermal stabilities, oxidative stabilities, estimation of product lifetimes, decomposition kinetics, effects of reactive atmospheres on materials, filler content of materials, moisture and volatile contents. TGA analysis was conducted to study the weight change of the sample in relative to temperature change under nitrogen atmosphere (Peterson, *et al.*, 2001; Sichina, n. d.).

TGA curve is plotted as a function of the weight loss versus temperature as shown in **Figure 3.16**. PE degraded in a single smooth step, where the range of decomposition is from 180^{o}C to 593^{o}C. Based on the derivative curve, the derivative peak temperature (DT_P) is noted at 487^{o}C and this value is similar to the value reported by Marcilla *et al.* (2005) which is 470^{o}C. The onset temperature (T_{onset}) for PE is noted at 455^{o}C. Only less than 0.5% weight of residue is obtained at the end of the degradation process and this indicates that the PE is fairly pure.

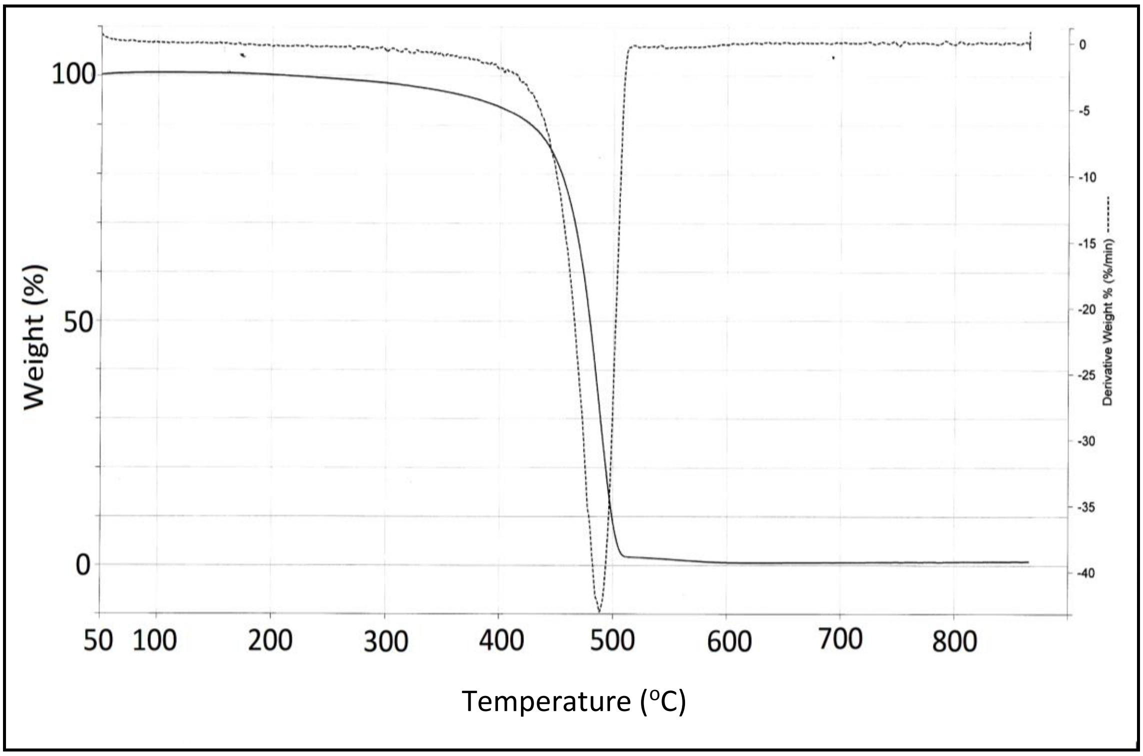

Figure 3.16: Thermogram of PE-**CI[1]**

c) Differential scanning calorimetric (DSC)

Differential Scanning Calorimetry (DSC) measures the temperature and heat flow associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity.

DSC analysis was performed by heating from 50 – 200^{o}C and allow to anneal for 10 minutes before the samples were cooled back to 50^{o}C and reheated to 200^{o}C. **Figure 3.17** shows DSC curves of PE-**CI[1]** that prepared at Cr/Al molar ratio of 26.2. DSC curves for PE-**CI[1]** prepared at the variation of Al/Cr molar ratio, PE-**CI[2]**, PE-**CI[3]** and PE-**CI[5]** are attached in the **Appendix**.

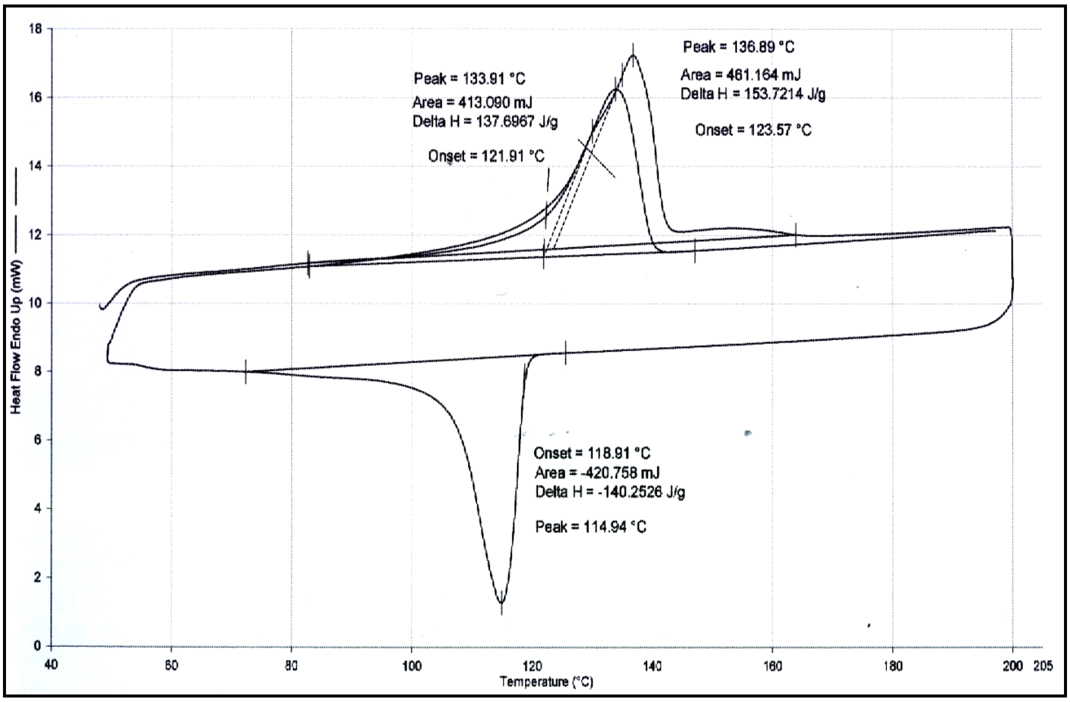

Figure 3.17: DSC scan of PE-**CI[1]** (Cr/Al = 26.2)

The first heating is eliminate some impurities in PE samples. The difference in melting temperature in the first heat and the second heat is only ~3°C which indicates that all PE samples were fairly pure. A small shoulder in the endothermic curve of first heat is found to be absent, thus supporting the elimination of some smidgen impurities.

The endothermic curve of second heat shows that the melting point for PE is noted at 131 – 137°C region. From the literature, the melting point for HDPE is at ~131°C and is in complete agreement with the in-situ x-ray diffraction measurements, where the disappearance of the crystalline Bragg peaks is observed between 130°C and 135°C (Manivannan & Seehra, n.d.; Tsukame *et al.*, 1997; Zaydouri & Grivet, 2009). The melting point for LDPE is 105°C (Tajeddin, *et al.*, 2009). It is believed that, the PE obtained from the polymerization was a high density polyethylene (HDPE).

Table 3.9: DSC data for PE-**CI[1]** at various of Al/Cr molar ratios

Al/Cr ratio	**First heating**		**Second heating**		**Cooling**	
	T_m (ºC)	**ΔH_m (J/g)**	**T_m (ºC)**	**ΔH_m (J/g)**	**T_c (ºC)**	**ΔH_c (J/g)**
11.2	139.1	149.1	135.6	101.9	114.4	-108.1
26.2	136.9	153.7	133.9	137.7	114.9	-140.3
30.0	134.5	147.9	132.8	139.2	112.8	-146.0
33.7	134.6	154.3	131.9	156.1	112.9	-170.3

Table 3.10: DSC data of PE produced by different catalysts

Catalysts	**First heating**		**Second heating**		**Cooling**	
	T_m (ºC)	**ΔH_m (J/g)**	**T_m (ºC)**	**ΔH_m (J/g)**	**T_c (ºC)**	**ΔH_c (J/g)**
CI[1]	136.9	153.7	133.9	137.7	114.9	-140.3
CI[2]	140.5	149.1	137.6	136.1	110.4	-141.5
CI[3]	142.6	146.5	137.2	121.4	112.1	-119.6
CI[5]	137.0	152.2	134.1	140.3	113.8	-151.1

Table 3.11: Difference between T_m, T_c and the percentage of crystallinity for PE-**CI[1]** at various Al/Cr molar ratios

Al/Cr ratio	**Different T_m &T_c (ºC)**	**Percentage of Crystallinity (%)**
11.2	21.2	34.8
26.2	19.0	47.0
30.0	20.0	47.5
33.7	19.0	53.3

Table 3.12: Difference between T_m, T_c and the percentage of crystallinity for PE produced by different catalysts

Catalysts	Different T_m &T_c (°C)	Percentage of Crystallinity (%)
CI[1]	19.0	47.0
CI[2]	27.2	46.5
CI[3]	25.1	41.4
CI[5]	20.3	47.9

Table 3.9 shows the analysis of DSC curves for the PE-**CI[1]** produced at various Al/Cr molar ratios and **Table 3.10** shows the analysis of PE formed from different catalysts. Galovic, *et al.* (2012) suggested that the melting point is an indication of the crystallite size and perfection. An increase/decrease in the melting point implies larger/smaller crystallites and formation of more/less perfect crystallites. **Table 3.9** shows the melting point of PE-**CI[1]** increases as the Al/Cr molar ratio is lower. This indicates that the polymer becomes larger crystallites and more perfect crystallites at lower Al/Cr molar ratio. Meanwhile, **Table 3.10** shows that the melting points for PE-**CI[2]** and PE-**CI[3]** are higher than PE-**CI[1]** and PE-**CI[5],** indicating PE-**CI[2]** and PE-**CI[3]** have larger and more perfect crystallites compared to PE-**CI[1]** and PE-**CI[5]**.

By referring to exothermic curve, appearance of a huge peak indicate that the polymer releases an enormous amount of heat to break the hard crystalline arrangement at the crystallization temperature (Raghavendra *et al.*, n. d.). The crystallization temperature (T_c) is dependent on the type and length of the monomer block. Whereas, the enthalpy of crystallization (ΔH_c) would reflect the amount of such blocks in the polymers that are able to crystallize. Gan *et al.* (1985) reported that PE crystallites with greater stability hold the higher value of -ΔH_c and smaller difference between T_c, and T_m. **Table 3.9** shows the value of -ΔH_c becomes larger as the Al/Cr molar ratio is higher. This indicates that the crystallites of PE-**CI[1]** become more stable with higher Al/Cr molar ratio. However, the differences between T_c, and T_m show insignificant value as of Al/Cr molar ratio for PE-**CI[1]** is varied (**Table 3.11**).

Table 3.10 shows that higher values of -ΔH_c are observed in PE-**CI[1]** (ΔH_c = -140.3 J g^{-1}) and PE-**CI[5]** (ΔH_c = 151.1 J g^{-1}) compared to that of PE-**CI[3]** (ΔH_c= 119.6 J g^{-1}). Moreover, the difference between T_c and T_m for PE-**CI[3]** (25.1°C) is greater than PE-**CI[5] (**20.3°C) and PE-**CI[1]** (19.0°C) (**Table 3.12**). Therefore, the PE produced by Cr-based catalysts have greater stability compared to PE produced by mixed-metal (Cr-Fe) catalyst.

The percentage of crystallinity was summarized in **Tables 3.11** and **3.12**. PE-**CI[1]** (47.0%) and PE-**CI[5]** (47.6%) are found to formed highly crystalline polymer compared to PE-**CI[2]** (46.5%) and PE-**CI[3]** (41.4%). However, the higher Al/Cr molar ratio used in the polymerization system leads to the higher percentage of crystallinity of PE-**CI[1]**. The observation suggested that the percentage of crystallinity for PE is inversely proportional to the amount of Cr-metal in catalysts.

References

Aishah, M. J. (1995). *Synthesis of some chromium(III) carboxylates and the used of these complexes as Ziegler-Natta catalysts for the polymerization of ethylene.* Ph.D. dissertation, University of Malaya, Kuala Lumpur.

Alshaiban, A., & Soares, J. B. P. (2012). Effect of Hydrogen and External Donor on Propylene Polymerization Kinetics with a 4 th-Generation Ziegler-Natta Catalyst. *Macromolecular Reaction Engineering, 6*(6-7), 265-274.

Beatrice, M. D. S. B. (2009). *Synthesis of chromium(III) carboxylate complexes and their use in ziegler-natta polymerization.* M.Sc. dissertation, University of Malaya, Kuala Lumpur.

Billmeyer, F. W. (1984). *Textbook of polymer science* (3 ed.). New York: Wiley.

Blaine, R. L. (n. d.). Determination of Polymer Crystallinity by DSC. Retrieved from http://www.tainstruments.co.jp/application/pdf/Thermal_Library/Applications_Briefs/TA123.PDF

Boor, J. (1979). *Ziegler-Natta catalysts and polymerizations*. New York: Academic Press.

Galovic, S., Secerov, B., Trifunovic, S., Milicevic, D., & Suljovrujic, E. (2012). A study of gamma-irradiated polyethylenes by temperature modulated differential scanning calorimetry. *Radiation Physics and Chemistry, 81*(9), 1374-1377.

Gan, S. N., Aishah, M. J., & Ooi, C. P. (2000). Trinuclear oxo-centered chromium(III) carboxylate complexes as Ziegler-Natta catalysts for ethylene polymerization. In T. Sano, Uozumi, T., Nakatani, H and Terano, M. (Ed.), *Progress and Development of Catalytic Olefin Polymerization* (pp. 25-32). Tokyo: Technology and Education Publishers.

Gan, S. N., Burfield, D. R., & Soga, K. (1985). Differential scanning calorimetry studies of ethylene-propylene copolymers. *Macromolecules, 18*(12), 2684-2688.

Gan, S. N., Chen, S. I., Ohnishi, R., & Soga, K. (1987). Homo- and copolymerization of ethylene and propylene using a heterogeneous chromium catalyst system. Polymer, vol 28, 1391-1395. *Polymer, 28*, 1391-1395.

Gan, S. N., Chen, S. I., Rikuo Ohnishi, & Soga, K. (1984). Homo- and co-polymerization of ethylene and propylene by using a new chromium catalyst. *Die Makromolekulare Chemie, Rapid Communications, 5*(9), 535-539.

Hagemann, H., Snyder, R. G., Peacock, A. J., & Mandelkern, L. (1989). Quantitative infrared methods for the measurement of crystallinity and its temperature dependence: polyethylene. *Macromolecules, 22*(9), 3600-3606.

Huang, J., & Rempel, G. L. (1995). Ziegler-Natta catalysts for olefin polymerization: Mechanistic insights from metallocene systems. *Progress in Polymer Science, 20*(3), 459-526.

Jones, W. R., & Lauer, J. L. (1979). INFRARED ANALYS IS OF POLYETHYLENE WEAR SPECIMENS US ING ATTENUATED TOTAL REFLECTION SPECTROSCOPY. *NASA Technical Memorandum 79228*. Retrieved from http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19790021158_1979021158.pdf

Keii, T. (1972). *Kinetics of Ziegler-Natta polymerization*. Tokyo: Kodansha.

Kissin, Y. V. (1985). *Isospecific polymerization of olefins with heterogenous Ziegler-Natta catalysts*. New York: Springer-Verlag.

Kong, Y., & Hay, J. N. (2002). The measurement of the crystallinity of polymers by DSC. *Polymer, 43*(14), 3873-3878.

Krimm, S. C. Y. L., and G. B. B. M. Sutherland. (1956). Infrared Spectra of High Polymers. II. Polyethylene. *The Journal Of Chemical Physics, 25*(3), 549 - 562.

Manivannan, A., & Seehra, M. S. (n.d.). IDENTIFICATION AND QUANTIFICATION OF POLYMERS IN WASTE PLASTICS USING DIFFERENTIAL SCANNING CALORIMETRY. Retrieved from http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/42_4_LAS%20VEGAS_09-97_1028.pdf

Marcilla, A., García-Quesada, J. C., Sánchez, S., & Ruiz, R. (2005). Study of the catalytic pyrolysis behaviour of polyethylene–polypropylene mixtures. *Journal of Analytical and Applied Pyrolysis, 74*(1–2), 387-392.

Martin, H. (2007). *Polymers, patents, profits : a classic case study for patent infighting : Karl Ziegler, the team, 1953-1998*. Weinheim: Wiley-VCH.

McKenzie, I. D., Tait, P. J. T., & Burfield, D. R. (1972). Ziegler-Natta catalysis: 2. A kinetic investigation. *Polymer, 13*(7), 307-314.

Moore, W. R. (1963). *An Introduction to Polymer Chemistry*. London: University of London Press Ltd.

Natta, G., & Pasquon, I. (1959). The Kinetics of the Stereospecific Polymerization of α-Olefins. In P. W. S. D.D. Eley & B. W. Paul (Eds.), *Advances in Catalysis* (Vol. Volume 11, pp. 1-66): Academic Press.

Ooi, C. P. (1996). *The use of trinuclear chromium(III) complexes as Ziegler-Natta catalysts for the polymerization of ethylene.* M.Sc. dissertation, University of Malaya, Kuala Lumpur.

Peterson, J. D., Vyazovkin, S., & Wight, C. A. (2001). Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene). *Macromolecular Chemistry and Physics, 202*(6), 775-784.

Raghavendra R. Hegde, M. G. Kamath, & Dahiya, A. (n. d.). POLYMER CRYSTALLINITY. Retrieved from http://web.utk.edu/~mse/Textiles/Polymer%20Crystallinity.htm

Rojas, B. G., Fatou, J., Martinez, C., & Laguna, O. (1997). The characterization of high-density polyethylenes functionalized with diethylmaleate: Correlation between FT-IR and 13C NMR data. *European Polymer Journal, 33*(5), 725-728.

Shamiri, A., Hussain, M. A., Mjalli, F. S., & Mostoufi, N. (2010). Kinetic modeling of propylene homopolymerization in a gas-phase fluidized-bed reactor. *Chemical Engineering Journal, 161*(1-2), 240-249.

Sichina, W. J. (2000a). Better Means of Determining Polymer Crystallinities by DSC: Temperature Dependent Crystallinity Software. *THERMAL ANALYSIS application note*. Retrieved from www.thermalsupport.com/filemanager/file_download.php?fi=37

Sichina, W. J. (2000b). DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics. *THERMAL ANALYSIS application note*. Retrieved from www.thermalsupport.com/filemanager/file_download.php?fi=21

Sichina, W. J. (n. d.). Characterization of Polymers Using TGA. *THERMAL ANALYSIS application note*. Retrieved from http://depts.washington.edu/mseuser/Equipment/RefNotes/TGA_Notes.pdf

Soga, K., Chen, S. I., Shiono, T., & Doi, Y. (1985a). Homo- and copolymerization of ethylene and propylene with a soluble chromium catalyst. *Polymer, 26*, 1888-1890.

Soga, K., Chen, S. I., Shiono, T., & Doi, Y. (1985b). Preparation of highly active Cr-catalysts for ethylene polymerization. *Polymer, 26*, 1891-1894.

Tajeddin, B., Rahman, R. A., Abdulah, L. C., Ibrahim, N. A., & Yusof, Y. A. (2009). Thermal properties of low density polyethylene - Filled kenaf cellulose composites. *European Journal of Scientific Research*, *32*(2), 223-230.

Tan, S. H. (2007). *Synthesis of chromium(III) acetate and chloroacetate complexes and their application in olefin polymerization.* Unpublished M.Sc. dissertation, University of Malaya, Kuala Lumpur.

Tatizawa, N., & Quijada, R. (1992). Propene polymerization using ziegler-natta catalyst supported on modified magnesium oxide. *European Polymer Journal, 28*(2), 139-143.

Tsukame, T., Ehara, Y., Shimizu, Y., Kutsuzawa, M., Saitoh, H., & Shibasaki, Y. (1997). Characterization of microstructure of polyethylenes by differential scanning calorimetry. *Thermochimica Acta, 299*(1–2), 27-32.

Wong, J. X. (2010). *Synthesis of chromium-based Ziegler-Natta catalysts and thier application in ethylene polymerization and copolymerization.* Unpublished M.Sc. dissertation, University of Malaya, Kuala Lumpur.

Zaydouri, A., & Grivet, M. (2009). The effect of electron irradiation on high-density polyethylene: Positron annihilation lifetime spectroscopy, differential scanning calorimetry and X-ray scattering studies. *Radiation Physics and Chemistry*, *78*(9), 770-775.