CHAPTER 4

RESULTS AND DISCUSSION : ETHYLENE AND PROPYLENE POLYMERIZATION

4.1 Chromium(III) Monocholoroacetate, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ As Ziegler-Natta catalyst

Chromium(III) monochloroacetate was synthesized by refluxing commercial chromium nitrate nonahydrate with chloroacetic acid. Preparation method of this complex had been described in Chapter 2, Section 2.1.2 (a).

The percentage of chromium in this complex as determined by titrimetric method and was 17.3%. Weight loss in TGA thermal analysis curve showed that 3 water of hydration were attached to the complex.

$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ complex was relatively stable towards air and moisture as compared to other Ziegler-Natta catalysts such as titanium and vanadium based catalysts. This complex in combination with diethylaluminium chloride ($AlEt_2Cl$) at various ratios produced different activity in ethylene polymerization. Reaction activity also varied with temperature. The overall polymerization rate increased when temperature increased to 29°C. At higher 36°C and 40°C, the polymerization rate dropped.

4.2 Diethylaluminium Chloride ($AlEt_2Cl$) As Cocatalyst

Diethylalumium chloride was prepared to the concentration of 0.1546M by diluting 2ml pure $AlEt_2Cl$ (97%) in 98ml toluene. The solution was kept in a stoppered bottle and was stored in the dry box. $AlEt_2Cl$ is sensitive to air and moisture thus extra care was needed when preparing the solution. In ethylene polymerization, diethylaluminium chloride was combined with chromium (III) monochloroacetate complex in the presence of toluene solvent to form a heterogeneous catalyst system. The Al/Cr ratio varied in the range of 20.8 - 42.2.

4.3 Typical Ethylene Polymerization Process

Polymerization was carried out in a round-bottom reaction flask connected to the gas line as shown in Figure 3.1. The setup has a constant volume, V = 2997ml. Tap C, which leads to the reaction flask was opened after the reaction reservoirs and gas line were filled with monomer gas. Subsequently, a drop in monomer gas pressure was noted as the gas filled the reaction flask and dissolved into toluene. The stopwatch was started and the corresponding pressure was taken as the initial pressure of the polymerization reaction.

A separate experiment with the absence of catalyst and cocatalyst was carried out as a control to determine the pressure drop for 100 ml pure toluene to be saturated with monomer. Correction of pressure readings was made during the calculation of actual pressure drop by deducting the pressure in control run from the pressure drop obtained during polymerization.

The kinetic of polymerization was monitored by measuring the pressure drop of monomer against time using the mercury manometer on the gas line. The amount of monomer being consumed during the reaction was calculated from the ideal gas law, $\Delta n = (\Delta P \times V) / RT$ where ΔP is the pressure drop, V refers to the constant volume, 2997ml, R is the Universal gas constant and T is the monomer gas temperature which was the average room temperature during the experiment. The catalytic activity of a polymerization run is expressed as the amount of polymer formed per g of Cr per hour per 1 atm monomer pressure.

Table 4.1 shows the kinetic data of a typical ethylene polymerization reaction. Chromium(III) monochloroacetate, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ catalyst system was used where %Cr = 17.3%. 0.0197g chromium complex was mixed with 87ml toluene and 13ml diethylaluminium chloride as cocatalyst. The Al/Cr ratio was 30.8. The mixture was left to 'age' for 15 minutes. Polymerization was then carried out at reactor temperature for 60 minutes. Column 2 in Table 4.1 shows the manometer readings in unit of cmHg. Pressure drop during control run was shown in column 3 while column 4 indicates the actual pressure drop.

Table 4.1: Kinetic of a typical ethylene polymerization reaction

Time/ min	Manometer reading/ cmHg	Pressure drop (during reaction)/cmHg	Pressure drop (control run)/ cmHg	Actual pressure drop/ cmHg	Catalytic activity/ gPE/gCr/hr/atm
0.0	81.85	0.00	0.00	0.00	0
0.5	80.50	2.70	1.50	1.20	1768
1.0	79.90	1.20	0.90	0.30	149
1.5	79.55	0.70	0.60	0.10	450
2.0	79.35	0.40	0.30	0.10	151
2.5	79.20	0.30	0.20	0.10	151
3.0	79.10	0.20	0.10	0.10	151
3.5	79.05	0.10	0.00	0.10	151
4.0	78.95	0.20	0.10	0.10	151
4.5	78.90	0.10	0.00	0.10	152
5.0	78.85	0.10	0.00	0.10	152
5.5	78.80	0.10	0.00	0.10	152
6.0	78.75	0.10	0.00	0.10	152
6.5	78.70	0.10	0.00	0.10	152
7.0	78.65	0.10	0.00	0.10	152
7.5	78.60	0.10	0.00	0.10	152
8.0	78.55	0.10	0.00	0.10	152
8.5	78.50	0.10	0.00	0.10	152
9.0	78.45	0.10	0.00	0.10	152
10.0	78.35	0.20	0.00	0.20	153
11.0	78.25	0.20	0.00	0.20	153
12.0	78.20	0.10	0.00	0.10	76
13.0	78.15	0.10	0.00	0.10	76
14.0	78.10	0.10	0.00	0.10	77
16.0	78.00	0.20	0.00	0.20	77
18.0	77.90	0.20	0.00	0.20	77
20.0	77.80	0.20	0.00	0.20	77
22.0	77.70	0.20	0.00	0.20	77
24.0	77.60	0.20	0.00	0.20	77
26.0	77.45	0.30	0.00	0.30	116
28.0	77.35	0.20	0.00	0.20	77
30.0	77.25	0.20	0.00	0.20	77
35.0	77.05	0.40	0.00	0.40	62
40.0	76.90	0.30	0.00	0.30	47
50.0	76.60	0.60	0.00	0.60	47
60.0	76.35	0.50	0.00	0.50	39

Polymerization conditions:

Catalyst system = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$

Al/Cr ratio = 30.8, gas temperature = 29°C, reactor temperature = 29°C,

aging time = 15 minutes, reaction time = 60 minutes,

volume = 2997 ml, solvent = toluene

Chromium catalyst and diethylaluminium cocatalyst were added under nitrogen atmosphere and were allowed to 'age' for 15 minutes before the monomer was being introduced. During the aging, the colour of Cr catalyst would change from green to yellowish orange. This was due to the reduction of Cr^{3+} to Cr^{2+} which was the active state for polymerization[1-3]. At the end of the polymerization, colour of the reaction mixture remained orange indicated that the active Cr^{2+} still present in the solution.

The catalytic activity versus time for ethylene polymerization using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system was shown in Figure 4.1. The Al/Cr molar ratio used in this reaction was 30.8 and the reaction temperature was 29°C. The kinetic curve obtained was of the decay type[4]. A decay- type polymerization curve is typical for high activity catalysts[5]. This type of kinetic curve was identified in the reaction of propylene polymerization using $\alpha TiCl_3/AlEt_3$ catalyst system by Coover[6] and in the polymerization of ethylene by Bier et al[7].

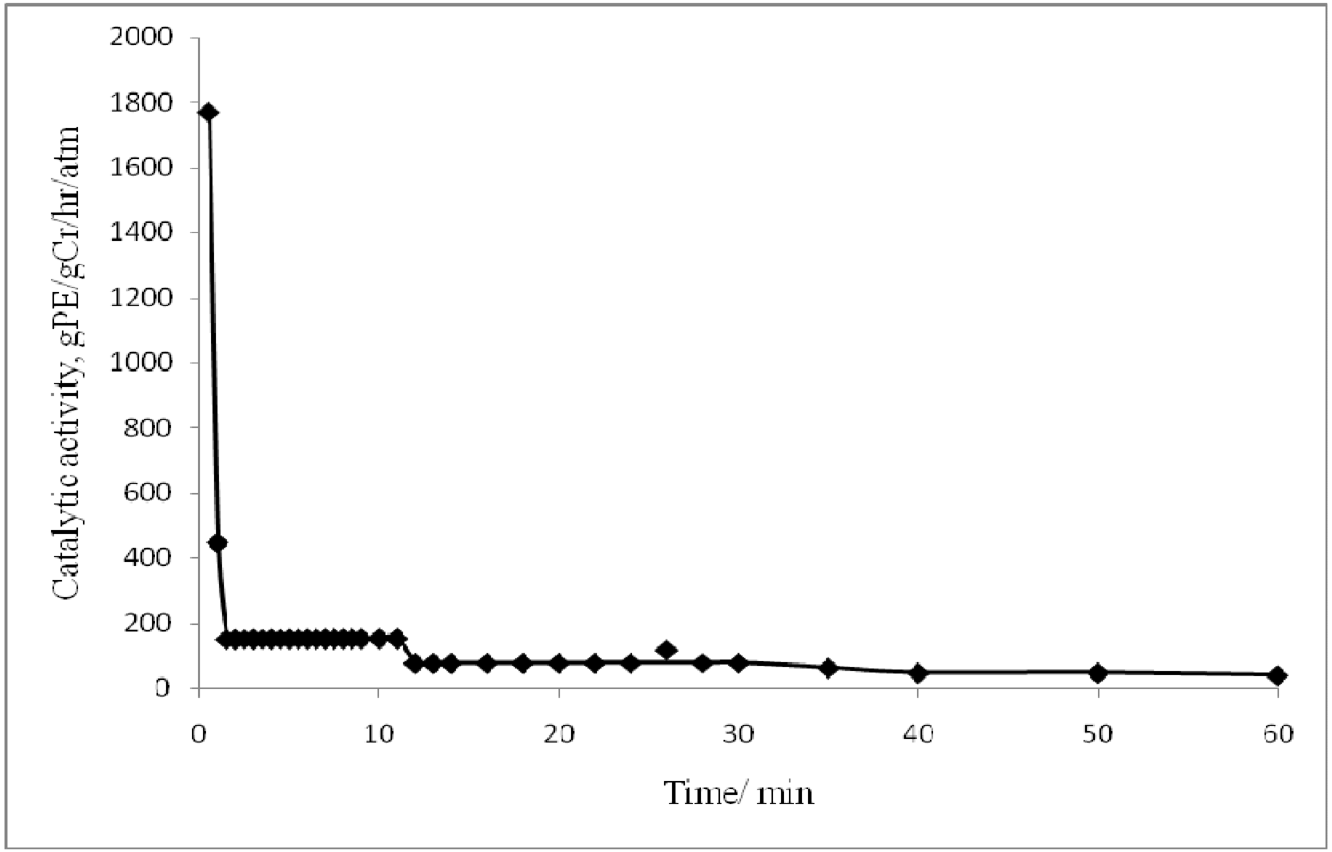


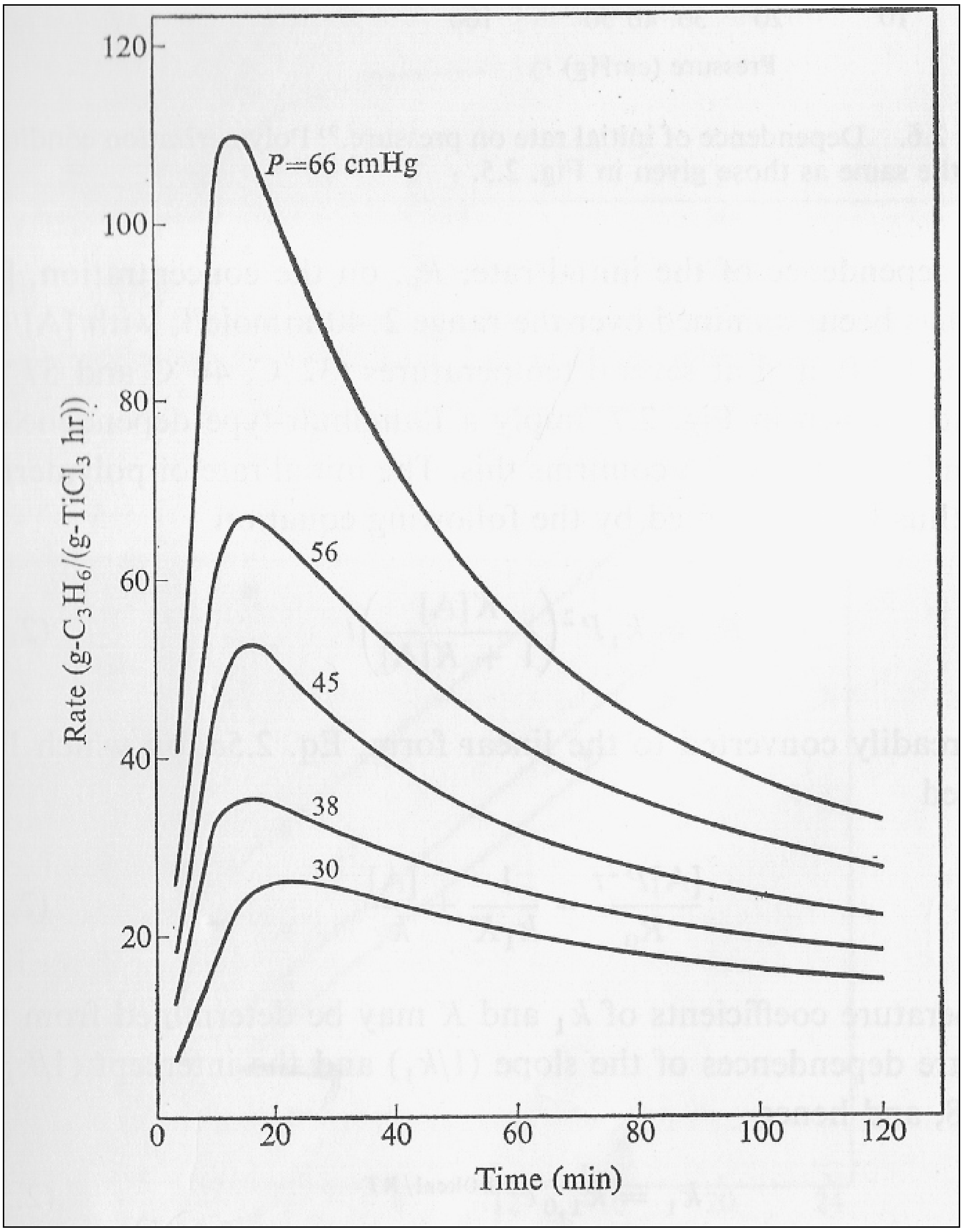
Figure 4.1: Kinetic curve of ethylene polymerization using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio= 30.8, temperature= 29°C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

Boor[8] noted that in a decay-type rate curve, there is an induction period before the maximum rate is reached, and the rate will decline to a steady state after the maximum rate. Second decay might also occur after the steady state. The induction period has been explained by Blais et al.[9] and a number of workers using $TiCl_3$ as catalyst. They assumed that crystals and aggregates of $TiCl_3$ are broken and ground under the growing polymer chain. Therefore the number of active sites would increase thus leading to higher reaction rate.

Keii et al.[10] studied the kinetics of propylene polymerization and found that the kinetic behavior during the induction period was affected by the order of addition of cocatalyst and monomer to $TiCl_3$ catalyst. Kinetic curves obtained were shown in Figure 4.2.

However in this study, no build-up or induction period was observed in the initial part of polymerization. The catalytic activity decreased rapidly to a constant value a few minutes after the reaction started. Second decay happened after 10 minutes of the stationary state. The rate declined at a slower pace. This further decrease might be due to the polymer accumulated around the active center thus slowing down the diffusion of monomer.

Boor[8] suggested that, at increased time of polymerization, the decline in rate becomes smaller. Varying the catalyst-monomer system would result in different rate of decline. Other factors that lead to the decrease in polymerization activity include a decrease in number of active centers and a lowering in activity of individual centers due to structural changes. Besides, as the polymerization goes on, viscosity of the solution would increase and caused the polymerization rate turned slower.



Polymerization conditions:

catalyst = 2 g TiCl$_3$/dm^3, cocatalyst = 15 mmol/ dm^3 AlEt$_3$/ in 250 cm^3 n-heptane

solvent = 250 ml n-heptane, temperature = 40 °C

Figure 4.2: Kinetic curves for propylene polymerization obtained at various monomer pressures[10]

Figure 4.3 shows the relationship between accumulative polyethylene yield with the reaction time. A linear correlation was obtained after 9 minutes the reaction started and it was due to the activation rate of the polymerization being the same with the deactivation rate. In a report published by McKenzie et al.[11], the linear portion in the plot indicated that the polymerization rate within a given run is first order with respect to the monomer.

Table 4.2: Polyethylene yield accumulated during reaction

Time/ min	Accumulative yield/ g
0.0	0.0000
1.0	0.0579
2.0	0.0757
3.0	0.0847
4.0	0.0936
5.0	0.1025
6.0	0.111
7.0	0.120
8.0	0.129
9.0	0.138
10.0	0.147
12.0	0.160
14.0	0.169
16.0	0.178
18.0	0.187
20.0	0.196
30.0	0.245
40.0	0.276
50.0	0.303
60.0	0.325

Polymerization conditions:

Catalyst system = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$

Al/Cr ratio = 30.8, gas temperature = 29°C, reactor temperature = 29°C,

aging time = 15 minutes, reaction time = 60 minutes

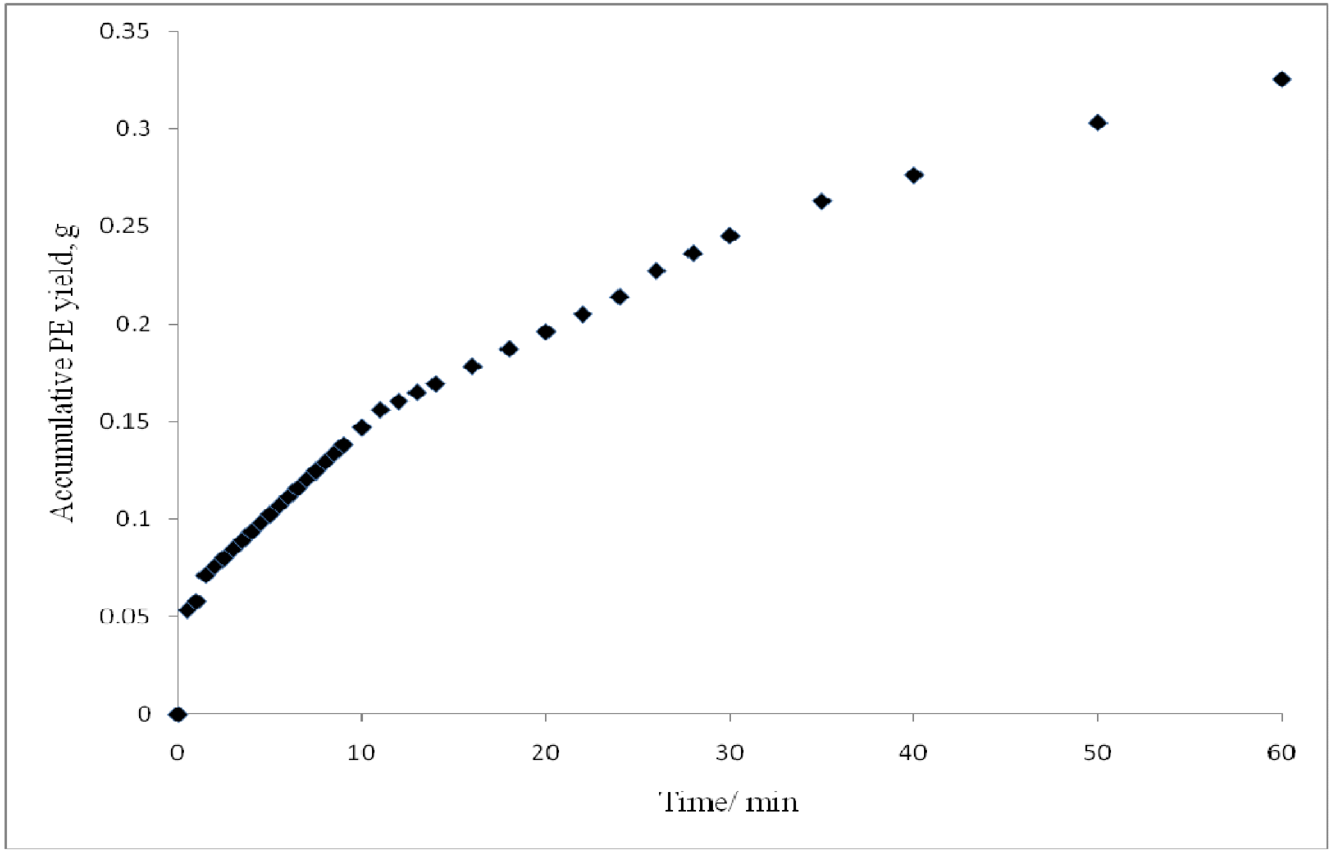


Figure 4.3: Plot of accumulative polyethylene yield versus reaction time using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 30.8, temperature 29 °C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

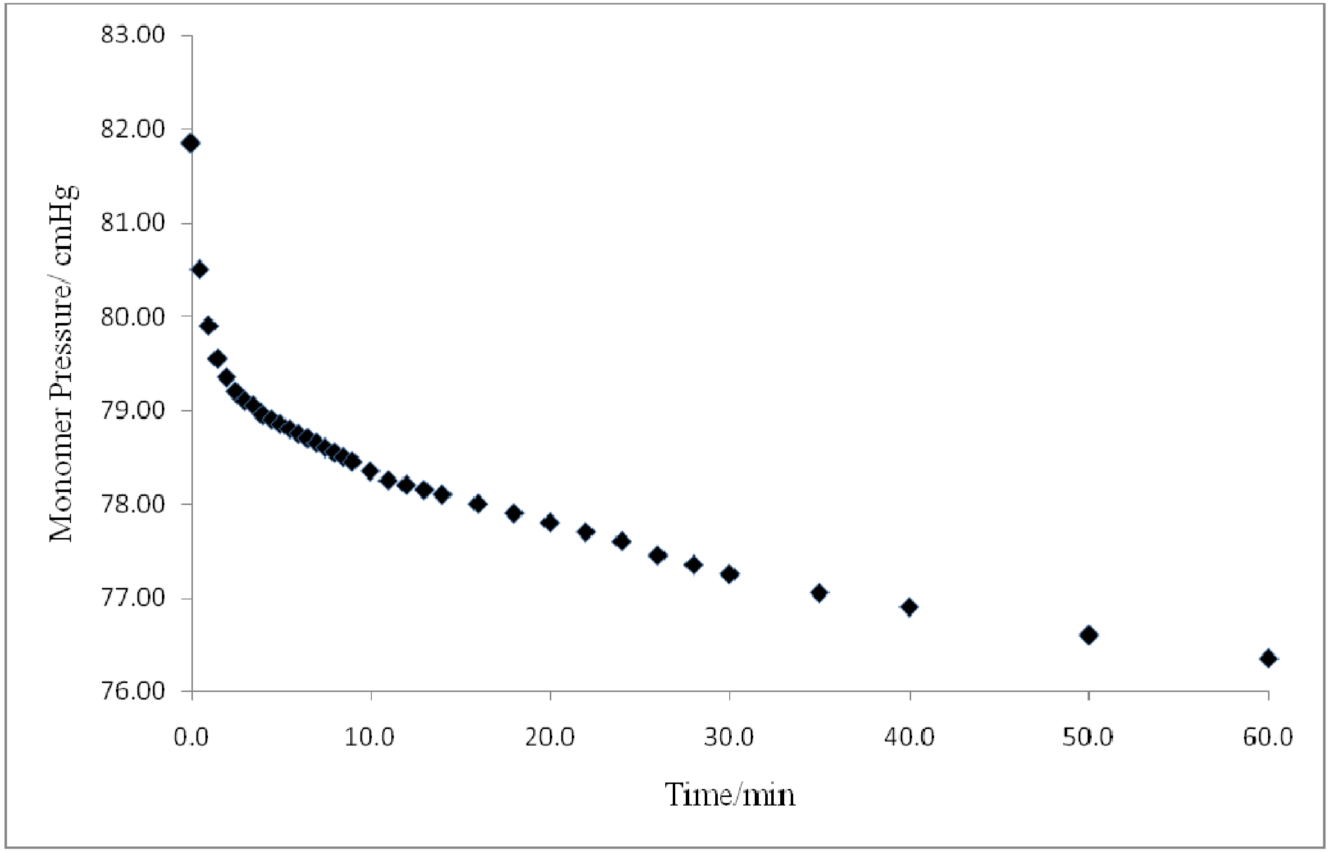


Figure 4.4: Plot of monomer pressure versus time using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 30.8, temperature 29 °C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

Monomer pressure drop, in cmHg was plotted as a function of time and was shown in Figure 4.4. The plot was linear at the initial stage of polymerization. The drop in pressure became smaller as the reaction progressed. This may be arise from the decrease in number of active centers and increased viscosity of the solution.

Polymerization of ethylene was carried out at various Al/Cr molar ratios. The obtained polymer yield was compared with the yield calculated from Ideal gas law. Table 4.3 summarizes the corresponding results. A graph of experimental yield versus calculated yield was plotted and it shows linear correlation. The difference between calculated yield and experimental yield could be due to the amount of monomer required to saturate the solvent. The result was illustrated in Figure 4.5.

Table 4.3: Correlation between pressure drop and polymer yield

Al/Cr ratio	Total pressure drop / cmHg	Calculated yield / g	Experimental yield / g
20.8	2.5	0.0755	0.0738
23.2	3.5	0.163	0.162
29.8	11.1	0.494	0.487
30.8	7.3	0.325	0.315
40.0	7.3	0.326	0.307
42.2	6.1	0.285	0.260

Polymerization conditions:

Catalyst system = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$,

gas temperature = 29°C, reactor temperature = 29°C, aging time = 15 minutes,

reaction time = 60 minutes, volume = 2997 ml, solvent= toluene

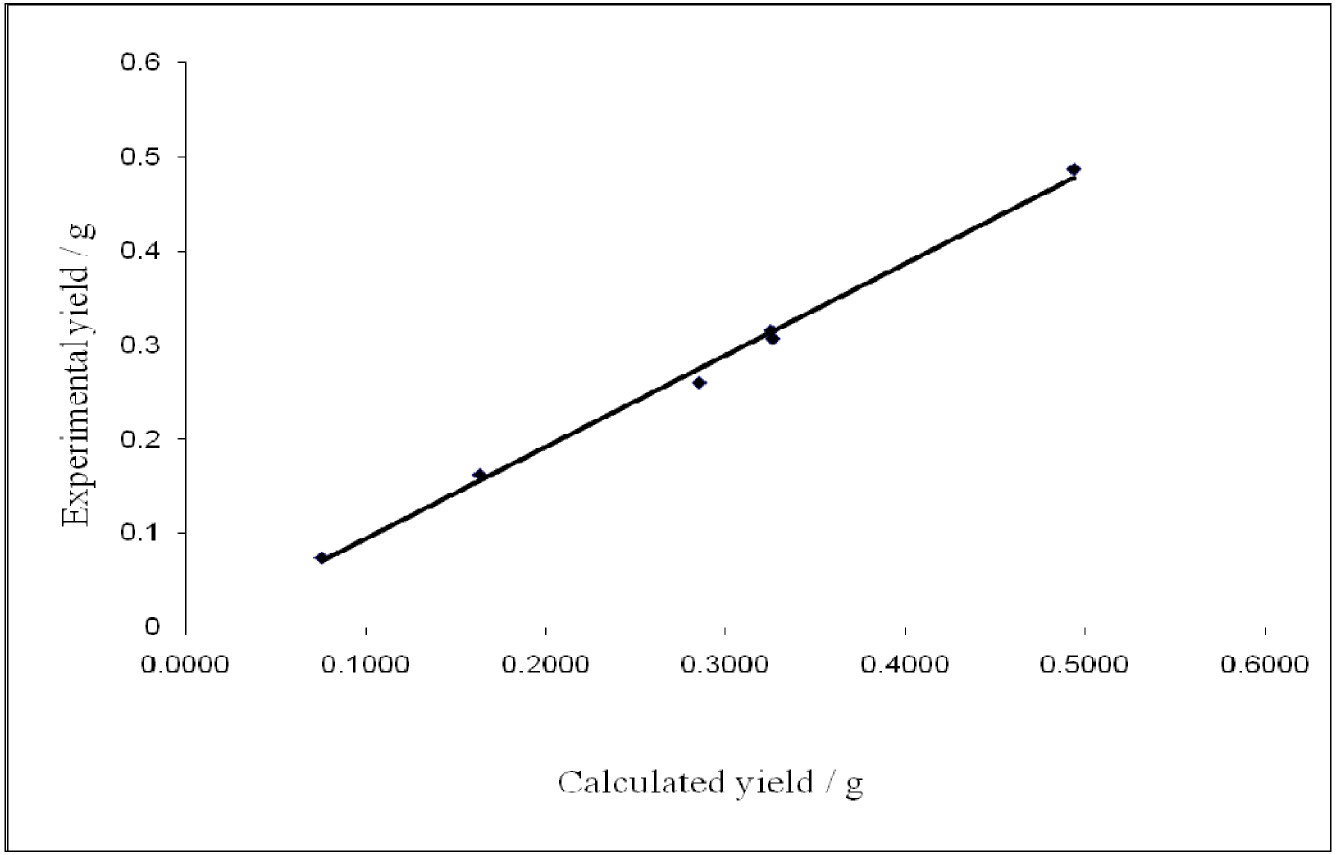


Figure 4.5: Plot of experimental yield versus calculated yield using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system, temperature 29 °C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

4.4 Kinetics of Polymerization

Polymerization of 4-methylpentene-1 using VCl_3/AlR_3 catalyst was investigated by Burfield et al.[12] and a scheme correlated the kinetics, molecular weight and active center data was proposed. They suggested that propagation step took place at an active center formed by the interaction of metal alkyl with the transition metal halide. The rate of propagation was expressed as:

$$R_p = k_p \theta_M C_o$$

where k_p refers to the propagation rate constant with respect to adsorbed monomer, C_o is the active centre concentration and θ_M is the fraction of the surface covered by adsorbed monomer. The rate of propagation depends on the number of active centers and the value of θ_M. The adsorption of monomer onto catalyst surface, θ_M can be described by the Langmuir- Hinshelwood isotherms,

$$\theta_M = \frac{K_M [M]}{1 + K_M [M] + K_A [A]}$$

where [M] is the concentrations of monomer, while K_M and K_A are the equilibrium constants for the equilibria.

Polymer chain growth occurred after the initiation had taken place. Novokshonova et al.[13] pointed out that the rate of chain initiation is much slower than that of chain propagation. Thus, two different types of active sites may exist in the polymerization systems. Propagating sites of concentration,C_o take part in the propagation step while potential sites of concentration, C_i are responsible for chain initiation. Potential sites are sites prior to initiation by monomer or sites arising from transfer reaction by either monomer or metal alkyl.

Assume that for a given concentration of transition metal halide, the maximum concentration of actives sites, C_t is constant. Therefore,

$$C_t = C_o + C_i$$

Polymer chain growth can be stopped if a transfer reaction occurs. Types of chain termination reactions include spontaneous disproportionation, transfer by monomer, transfer by base metal alkyl and inactivation of active centre.

The kinetic study of a typical polymerization run is closely related to ideal gas law, that is,

$$PV = nRT$$

where P is the monomer pressure, V is the volume, R is the Universal gas constant and T is the monomer gas temperature.

Under conditions of constant volume and temperature, the monomer pressure, P is directly proportional to the number of moles of ethylene monomer, n, as

$$P = \frac{nRT}{V}$$

Ethylene polymerization can be expressed as:

$$n\ CH_2{=}CH_2 \xrightarrow[k]{\text{catalyst}} -\!\left(CH_2\text{-}CH_2 \right)_n\!-$$

The rate law is,

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

where C is the molar ethylene monomer concentration and k is the rate constant.

In a closed system, the pressure, P is proportional to the molar monomer concentration, C.

$$C = \frac{n}{V}$$

therefore

$$P = CRT$$

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

$$= - k\, CRT$$

$$= - k\, P$$

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

integration of the above equation gives,

$$\ln P = -kt + c$$

For a first order reaction, a plot of ln P versus time should give a straight line. Polymerization reaction using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system follow this feature. The graph is shown in Figure 4.6.

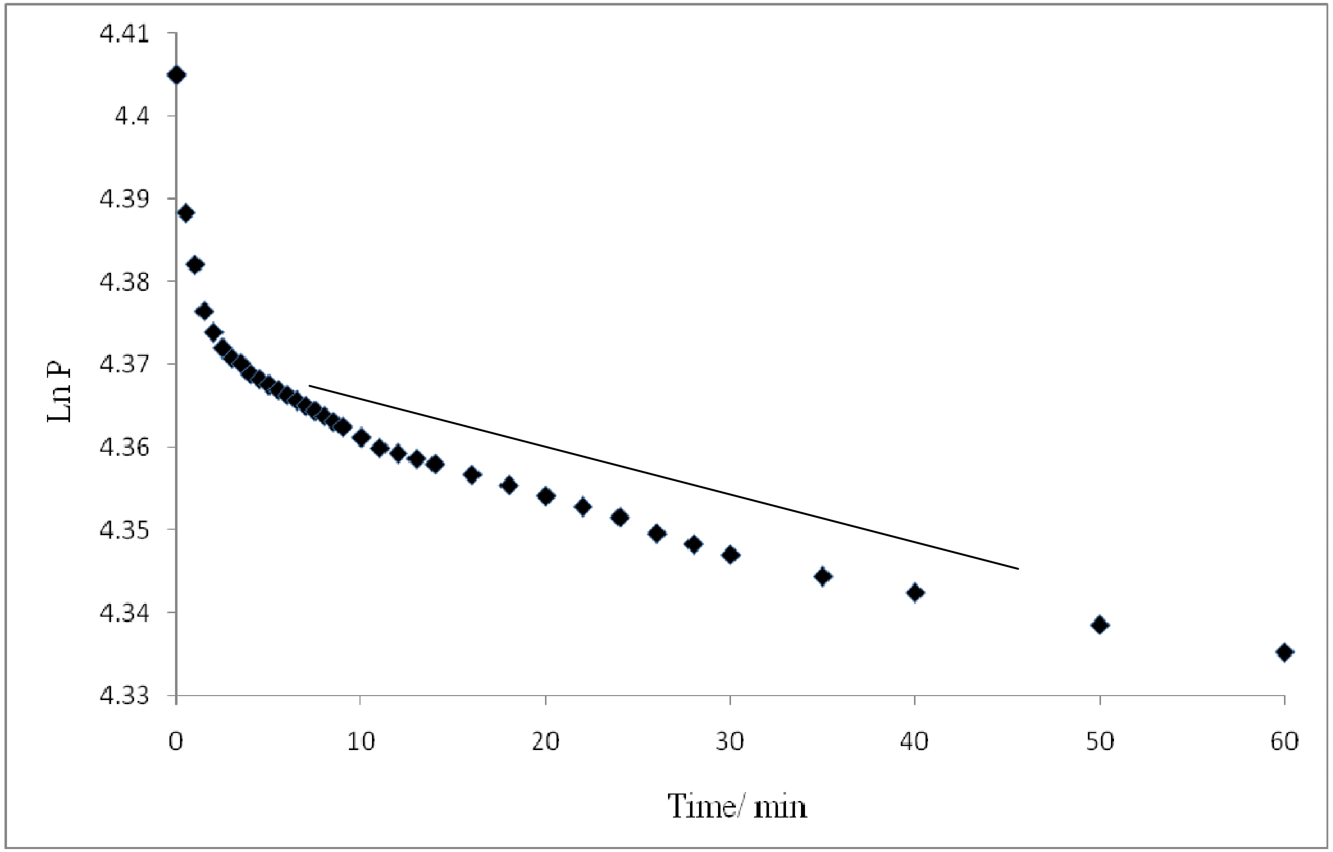


Figure 4.6: Plot of ln P versus time using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 30.8, temperature 29 °C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

4.5 Effect of Varying Al/Cr Ratio

In a typical polymerization run, the catalyst is activated with a cocatalyst before the monomer was being introduced into the reactor. The polymerization activity is largely dependent on the nature of the cocatalyst and the molar ratio of cocatalyst to catalyst. The influence of alkyl aluminium concentration on the polymerization kinetics had been studied by Natta and Pasquon[14] and they found difference in results when the $AlEt_3/TiCl_3$ ratio was varied from 1 to 8.5.

In this study, the effect of diethylaluminium cocatalyst to catalyst ratio was investigated by carrying out polymerization run at various Al/Cr ratios varied from 20.8 to 42.2. Concentration of the $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ catalyst was mantained constant throughout the whole series of run where approximately 0.020g chromium complex was used. The reactions were carried out at temperature= 29°C. Dependence of the catalytic activity on the Al/Cr ratio was illustrated in Figure 4.7.

Optimum activity was achieved with Al/Cr ratio at 30.8 where the maximum catalytic activity approached 1768 gPE/gCr/hr/atm. Drop in maximum initial activity was observed as the molar ratio of Al/Cr decreases fom 30.8 to 20.8. Lowering in the catalytic activity probably due to incomplete activation of the active centers. Gan et al.[15] reported at low Al/Cr ratios, a low spin Cr(II) complex was formed which was inactive for polymerization.

For polymerization run at low Al/Cr molar ratio of 20.8, polymerization reaction only occured for 40 minutes and there was no further drop in monomer pressure. This might be due to insufficient amount of aluminium alkyl present to activiate the catalyst centers.

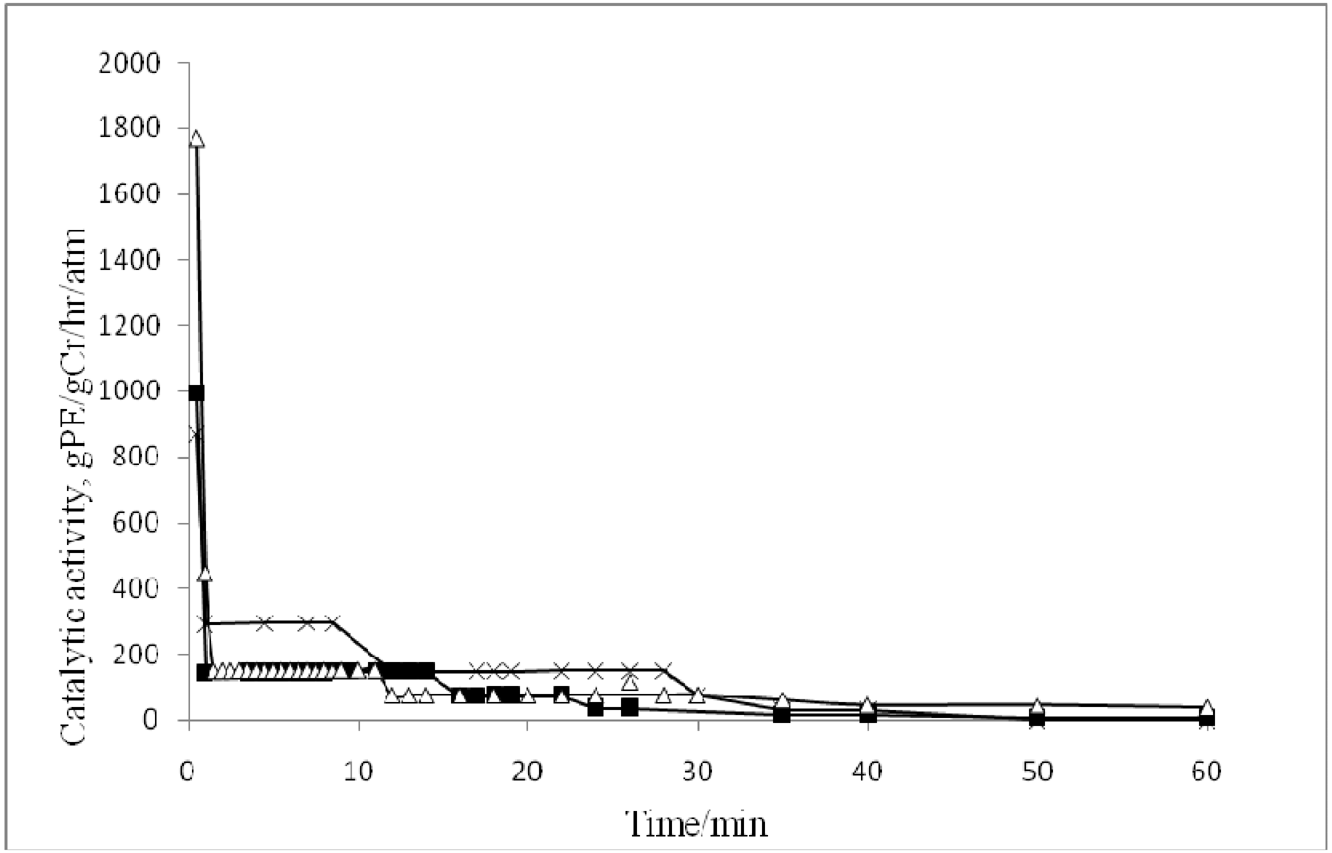


Figure 4.7: Kinetic curves of ethylene polymerization using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ / $AlEt_2Cl$ catalyst system at temperature=29 °C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene, ■, Al/Cr= 23.2; Δ, Al/Cr= 30.8; x, Al/Cr= 42.2

Further increase in the $AlEt_2Cl$ ratio above 30.8 has led to decrease in polymerization activity. McKenzie et al.[11] suggested that as the concentration of aluminium alkyl increases, transfer reactions become more significant and there is a possibility of a reversible active centers deactivation by adsorption of free aluminium alkyls. Besides, if the alkyl aluminium used is in excess with respect to the molar concentration of active centers, it might over reduce Cr to lower oxidation state and this would lead to decrease in activity.

Table 4.4: Maximum initial catalytic activity at various Al/Cr ratios

Al/Cr ratio	Maximum initial activity, gPE/gCr/hr/atm
20.8	868
23.2	992
28.6	1654
30.8	1768
32.3	1639
40.0	730
42.2	434

Polymerization conditions:

Catalyst system = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/ AlEt_2Cl$,

gas temperature = 29°C, reactor temperature = 29°C, aging time = 15 minutes

reaction time = 60 minutes, volume = 2997 ml, solvent= toluene

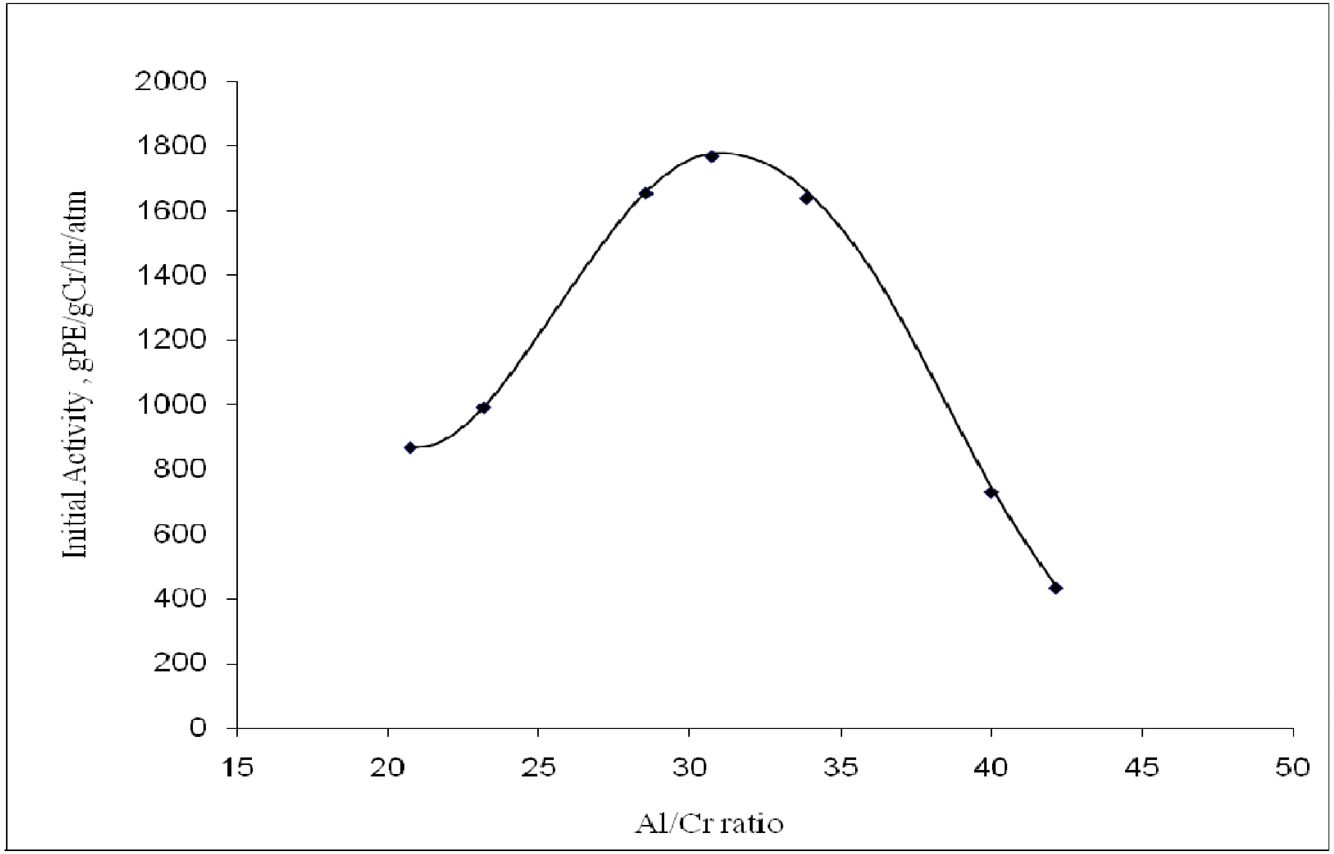


Figure 4.8: Plot of maximum initial activity versus Al/Cr ratio using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at temperature 29 °C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

4.6 Effect of Varying Polymerization Temperature

Reaction temperature plays an important role in the polymerization of ethylene and propylene[16-18].

Chromium (III) monochloroacetate complex and diethylaluminium chloride were used as catalyst system where Al/Cr molar ratio was maintained constant at 30. Mixture of catalyst and cocatalyst was allowed to ‘age’ for 15 minutes before the reaction was started. A number of ethylene polymerization run were carried out at different reaction temperature ranged from 18 to 40°C to study the rate of polymerization affected by the temperature. Results obtained were shown in Table 4.5.

The catalytic activity rose substantially with an increase temperature from 18 to 29°C. This was due to the steady state rate of polymerization increased with temperature. Figure 4.9 illustrated the kinetic curves of ethylene polymerization at various temperatures. The maximum rate obtained was 1768gPE/gCr/hr/atm and 0.315g polymer was producted. Further increase in temperature led to a drop in the activity of catalyst. Polymerization of ethylene at temperature 36°C and 40°C showed lower activity than that at 29°C. This phenomenon was explained by Keii et al.[19] that a decrease in the number of polymerization centers happened with increasing temperature. Comparison between polymerization activity at 29°C and 40°C was showed in Figure 4.10.

Berger and Grieveson[20] recognized a change in the kinetics from lower polymerization temperatures to higher polymerization temperatures, at which the activation energy changed from high to low. Therefore they supposed a change in the rate determining step from lower temperatures to higher temperatures. They also suggested that raising the temperature would decrease the solubility of the monomer in the solvent and cause it became too low to satisfy the potential polymerization activity of the catalyst thus a decline in activity is observed.

Based on the investigation of Zakharov et al.[21] that the number of growing chains increases with the temperature, Munoz-Escalona and Parada[22] believed that the decrease in the catalytic activity at high temperature was due to the overall lower mass transfer of the ethylene to the catalyst surface.

Table 4.5: Effect of various temperatures on maximum initial activity of ethylene polymerization

Temperature/ °C	Ratio Al/Cr	Maximum initial activity/ gPE/gCr/hr/atm	Ln initial activity	$1/T \times 10^{-3}$ K	Polymer yield/ g
18	29.9	737	6.60	3.45	0.210
22	30.8	1187	7.08	3.39	0.276
29	30.8	1768	7.48	3.31	0.315
36	29.8	1642	7.40	3.24	0.180
40	29.8	1635	7.40	3.20	0.160

<u>Polymerization conditions:</u>

Catalyst system = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/\ AlEt_2Cl$,

gas temperature = 29°C, aging time = 15 minutes

reaction time = 60 minutes, volume = 2997 ml, solvent= toluene

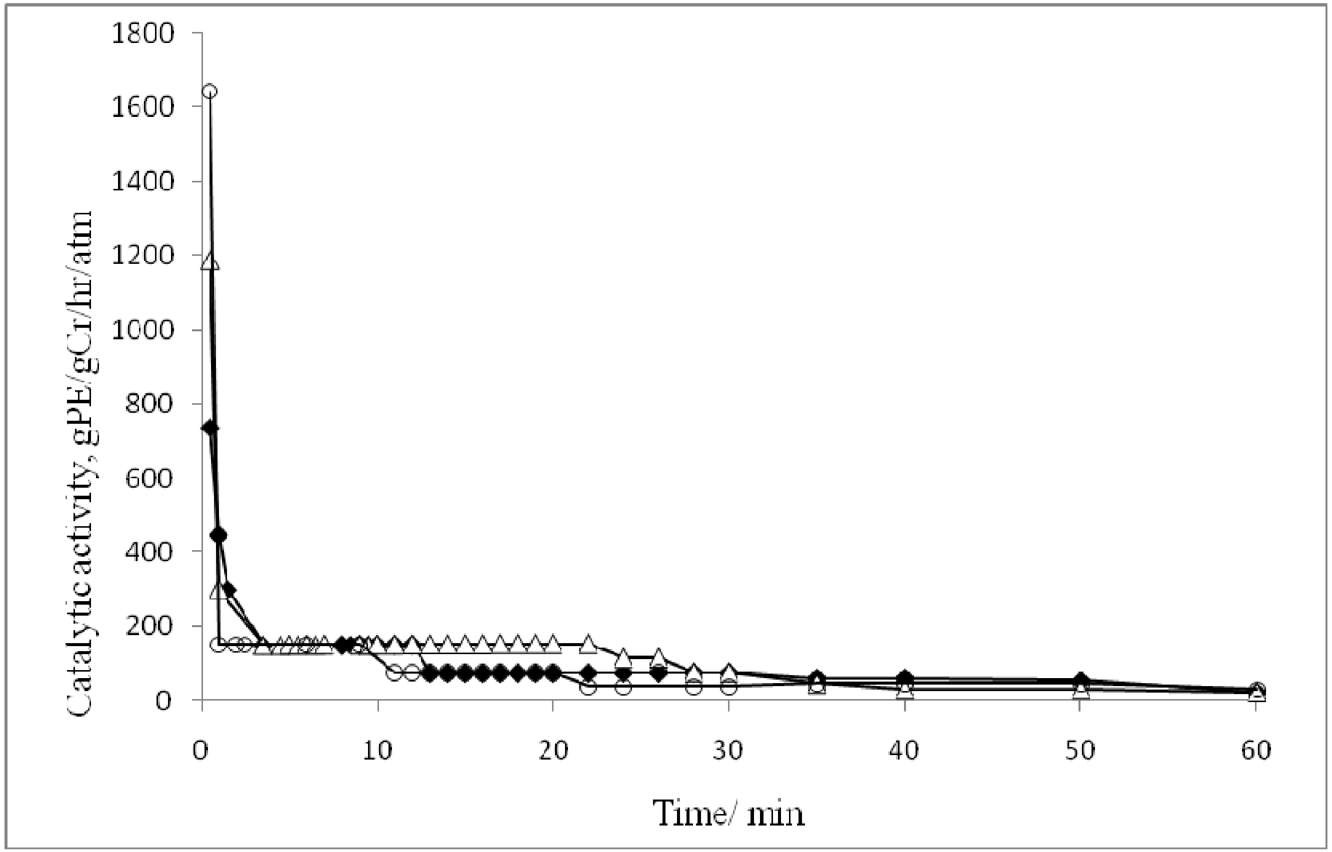


Figure 4.9: Kinetic curves of ethylene polymerization at various temperatures using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene, temperatures:◆ , T= 18°C; △, T= 22°C; ○, T= 36°C

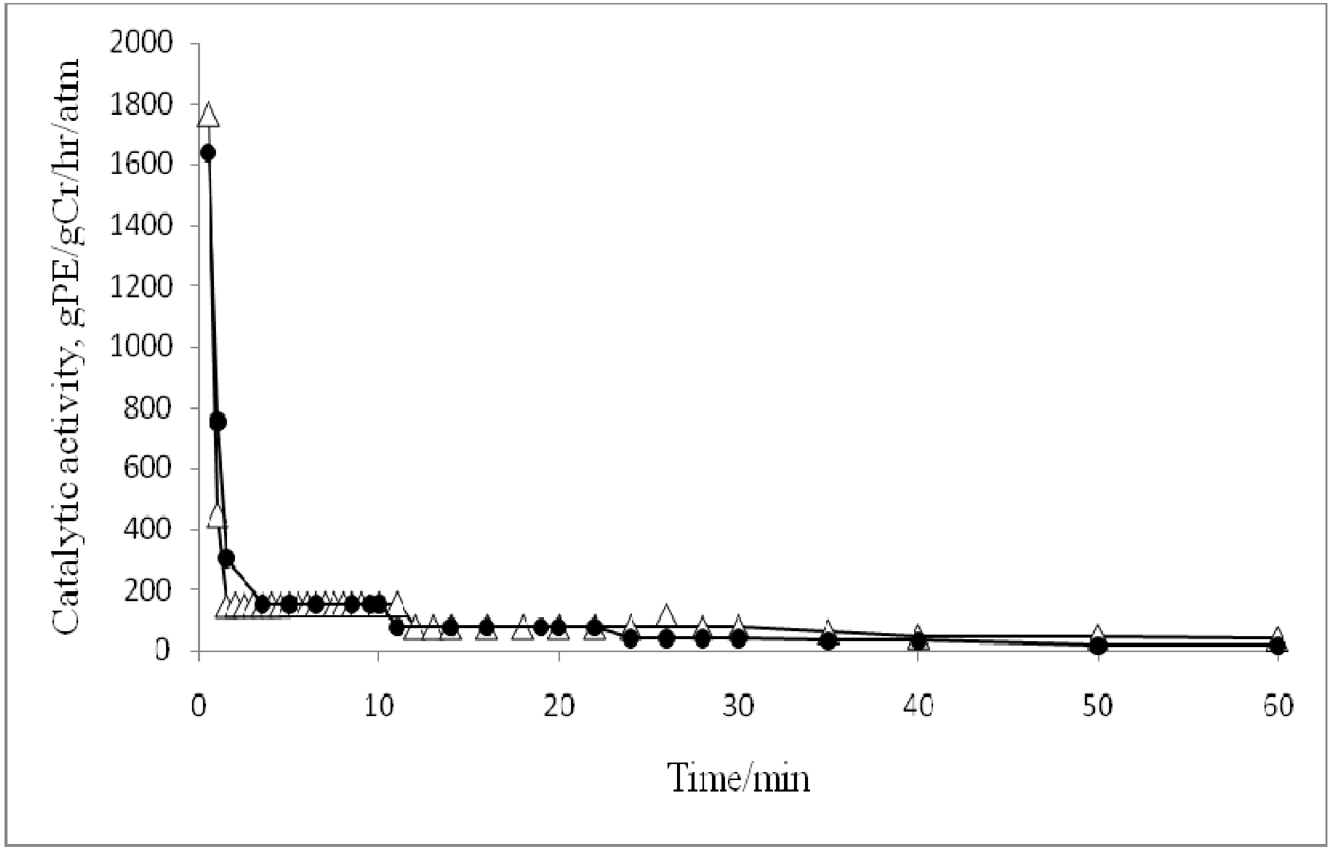


Figure 4.10: Kinetic curves of ethylene polymerization at various temperatures using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene, temperatures: △, T= 29°C; ●, T= 40°C

The kinetic curves obtained using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/$ $AlEt_2Cl$ catalyst system were of decay-type. The optimum temperature of polymerization depends on the structure and temperature stability of the catalyst components. The overall polymerization rate increased with an increase in the temperature up to 29°C. At higher temperature (36°C and 40°C), the active species became unstable and caused a drop in the polymerization rate.

The deactivation temperature activity of the catalyst can be described by Arrhenius equation where

$$k = A e^{-Ea/RT}$$

therefore,

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

where k is the rate constant, A is the Arrhenius constant, E_a is the activation energy, R is the gas constant and T is the temperature in Kelvin.

The activation energy, E_a can be obtained from Arrhenius plot. A plot of ln(initial activity) versus 1/T gives a straight line therefore Ea can be calculated from the slope. In this study, the activation energy was 25.19 kJ/mol^{-1}, which is comparable with the results reported by Keii[4], at which the activation energy for ethylene polymerization using titanium catalyst systems were in the range of 8-50 kJ/mol^{-1}.

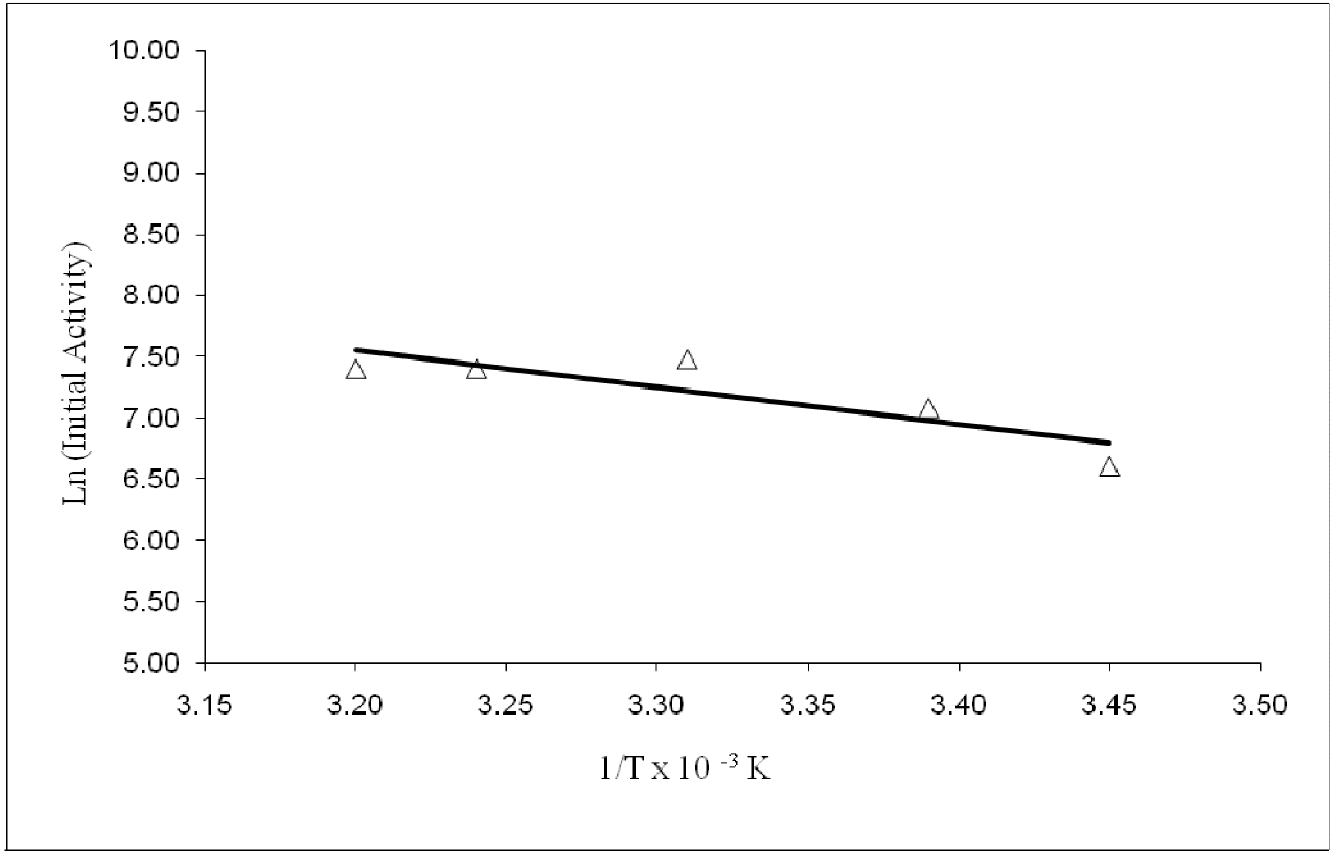


Figure 4.11: Arrhenius plot of ethylene polymerization using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system in the temperature range between 18°C - 40°C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

4.7 Effect of Chloro-Substituent Groups on Carboxylate

Choice of ligand used in preparing a catalyst is very important. Different ligands attached to the transition metal could vary the properties of the catalyst thus changes the polymerization rate and molecular weight distribution of the polymers produced.

Effect of chloro-substituent groups on chromium(III) carboxylate complexes were studied by carrying out polymerization of ethylene using differrent chromium(III) complexes in combination with diethylaluminium chloride under similar polymerization conditions. Al/Cr molar ratio was maintained constant at 29.5 ± 0.5 and mixture of catalyst and cocatalyst was allowed to react for 15 minutes before introducing ethylene monomer. The data obtained were summarized in Table 4.6.

Table 4.6: Catalytic activity and polyethylene yield obtained using a series of chromium(III) carboxylate complexes

Catalyst	Al/Cr ratio	Maximum Initial Activity/ gPE/gCr/hr/atm	Yield/ g
$[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$	29.3	1057	0.320
$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$	29.8	1548	0.487
$[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$	29.6	1573	0.572
$[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$	29.8	3116	0.544

<u>Polymerization conditions:</u>

Cocatalyst = $AlEt_2Cl$, gas temperature = 29°C, reactor temperature = 29°C,

aging time = 15 minutes, reaction time = 60 minutes,

volume = 2997 ml, solvent= toluene

Figure 4.12 shows the plots of maximum initial activity versus time for the catalysts. All four catalyst systems showed decay-type kinetic curves. The activity dropped to a steady-state a few minutes after the polymerization reaction started. Ethylene polymerization using chromium(III) trichloroacetate complex, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$ showed the highest activity among all other catalysts, with the maximum initial activity of 3116gPE/gCr/hr/atm and polymer yield 0.320g. Catalytic activity shown in the polymerization by chromium(III) dichloroacetate complex, $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ was 1573gPE/gCr/hr/atm, followed by chromium(III) monochloroacetate complex, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ and chromium(III) acetate with activity 1548gPE/gCr/hr/atm and 1057gPE/gCr/hr/atm respectively.

Results showed that the activity of chromium(III) acetate was much lower than catalysts with chloride substituted carboxylate groups. The maximum initial activity increased as the number of chlorine atom in the complexes increases. This was attributed to the electron withdrawing effect of the chlorine atoms. Tjaden and Jordan[23] found that metal alkyl reduces the transition metal carrying electron withdrawing substituents more rapidly than those having electron donating substituents. Chromium(III) trichloroacetate complex contained the highest number of chlorine atoms thus it was reduced most quickly by diethylaluminium chloride to generate the active sites.

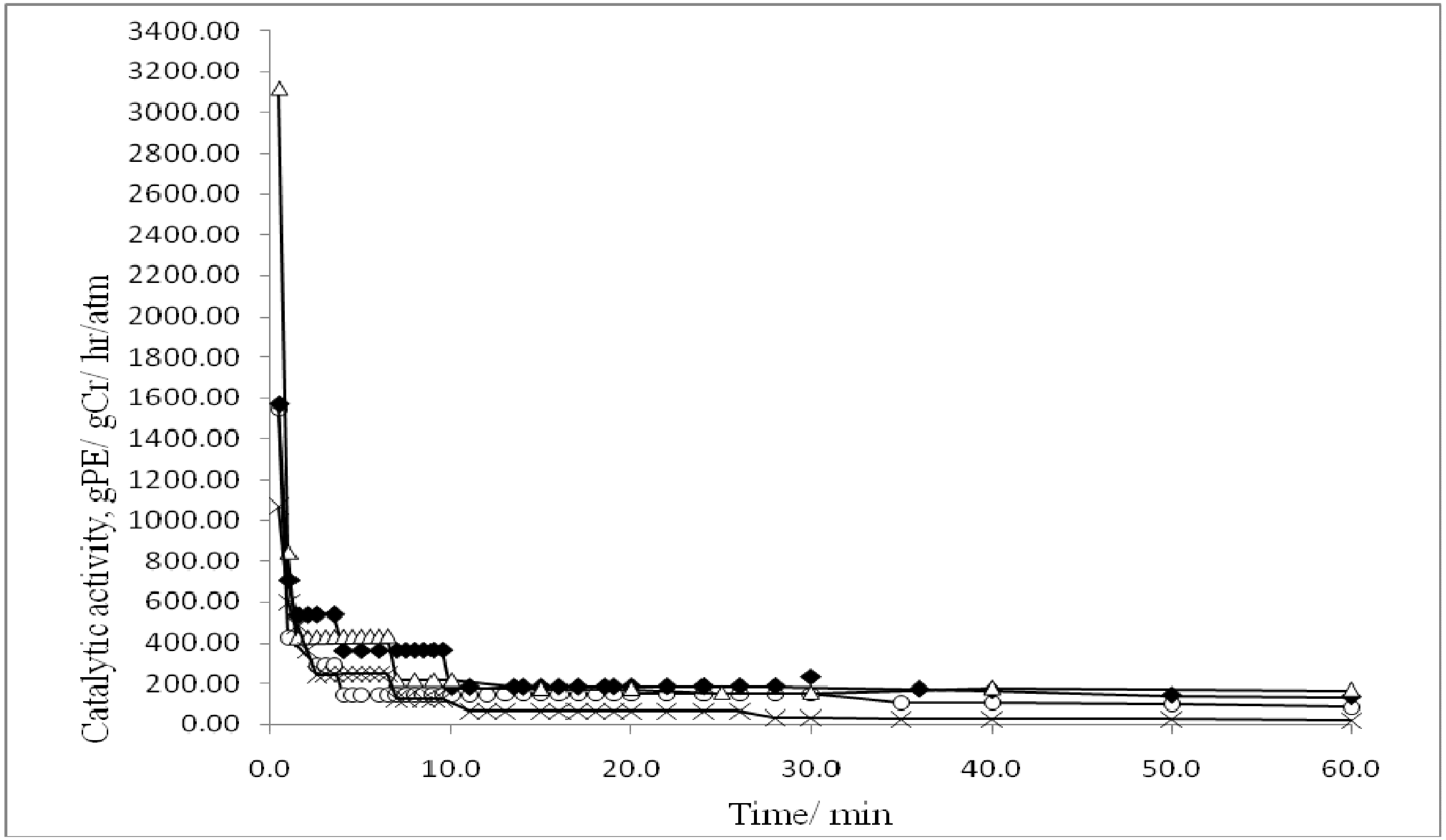


Figure 4.12: Kinetic curves of ethylene polymerization using different chromium(III) catalysts:

x, $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$; ○, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$;

◆, $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$; △, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$

Same observation was reported by Tajima and co-workers[24] on the polymerization of ethylene using $Ti(NMe_2)_nCl_{4-n}/AlEt_3$ systems. They found that the catalytic activity increased as the content of chloride increased. Data obtained were listed in Table 4.7.

Table 4.7: Polymerization with $Ti(NMe_2)_nCl_{4-n}/AlEt_3$ systems[25]

n	Catalyst system	Weight of polymer formed (g)
4	$Ti(NMe_2)_4$-$AlET_3$	6.4
3	$Ti(NMe_2)_3Cl$-$AlET_3$	9.7
2	$Ti(NMe_2)_2Cl_2$-$AlET_3$	12.1
1	$Ti(NMe_2)Cl_3$-$AlET_3$	18.3
0	$TiCl_4$-$AlET_3$	24.0

The order of increasing activity of the chloro-substituted carboxylate complexes in this study is as follows:

Complex 1 < Complex 2 < Complex 3 < Complex 4

where complex 1 = $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$;

complex 2 = $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$;

complex 3 = $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$;

complex 4 = $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$

4.8 Characterization of Polyethylene

(a) Infrared Spectroscopy

(i) Fourier Transform Infrared (FT-IR) Spectroscopy

Infrared spectroscopy has become one of the important techniques for the structural analysis of polymers. It detects the vibration characteristic of functional groups thus components in the sample can be determined. The intensity of absorption bands reflects the concentration of a functional group.

Two characteristic bands at 2926 and 2853 cm^{-1} are assigned as CH_2 asymmetric, $v_a(CH_2)$ and symmetric stretching modes[25], $v_s(CH_2)$. Bellamy[26] found that the intensities of the CH_2 stretching bands would increase as the polymer chain length increases.

The strong band appears at 1460 cm^{-1} is due to the bending mode of CH_2 group. The symmetrical deformation vibration mode of the hydrogen atoms has been shown to give rise to the band near 1375 cm^{-1}.[27] It is stable in position provided that the methyl group is attached to another carbon atom.

The rocking mode of the CH_2 group, $\gamma_r(CH_2)$ appears in the absorption band near 725 cm^{-1}, as shown by Sheppard and Sutherland[28]. The splitting of the $\gamma_r(CH_2)$ mode into two components at 721 cm^{-1} and 731 cm^{-1} is due to the interactions between adjacent molecules in the crystalline phase which results in both in-phase and out-phase rocking mode[29-30]. Similar effect was obtained in the CH_2 deformation vibration at 1460 cm^{-1}. However, doubling of the $\delta(CH_2)$ band only occurs in the solid state. In liquid state, the band appears single[31-32].

In this study, polyethylene samples were pressed into thin film. The films were scanned through FT-IR spectrometer and their spectra were recorded. Table 4.8 summarized the band assignments from infrared spectra of polyethylene obtained at various Al/Cr ratios.

Figure 4.13 shows the infrared spectrum of a polyethylene sample polymerized at Al/Cr ratio 23.2, with the use of $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system. The bands appeared at 2915 and 2848 cm^{-1} were assigned to asymmetric and symmetric CH_2 stretching modes. Absorption band at 1473 cm^{-1} was due to deformation of the CH_2 groups in the molecules. Splitting of the peak was observed at 1460 cm^{-1}.

The band at 1367 cm^{-1} indicated the symmetric terminal CH_3 deformation. This band appeared weak in all spectra. For polyethylene produced at Al/Cr 42.2, $\delta_s(CH_3)$ was observed at 1377 cm^{-1}. Krimm and co-workers[33], in the studies on single crystal of n-paraffins, assigned the 1369 cm^{-1} band as γ_w (CH_2) of planar zig-zag chain and the band at 1353 cm^{-1} and 1303 cm^{-1} as CH_2 wagging mode. However, these bands were not detectable in samples produced in this study.

Table 4.8: FT-IR band assignments of polyethylene obtained at various Al/Cr molar ratios

Polyethylene vibration mode (cm^{-1})		Al/Cr ratio				
		23.2	30.8	31.2	40.0	42.2
CH_2-stretching	Asymmetric	2915 *s*	2908 *s*	2922 *s*	2915 *s*	2918 *s*
	Symmetric	2848 *s*	2845 *s*	2851 *s*	2849 *s*	2849 *s*
CH_2- deformation		1473 *s*	1474 *s*	1474 *s*	1473 *s*	1472 *s*
		1460 *s*	1463 *s*	1463 *s*	1464 *s*	1463 *s*
Symmetric terminal CH_3- deformation		1367 *w*	1367 *w*	1367 *w*	1364 *w*	1377*w*
CH_2- rocking		731 *s*	730 *s*	731 *s*	730 *s*	730 *s*
		720 *s*	720 *s*	719 *s*	720 *s*	720 *s*

Abbrevations: *s* = strong; *w* = weak

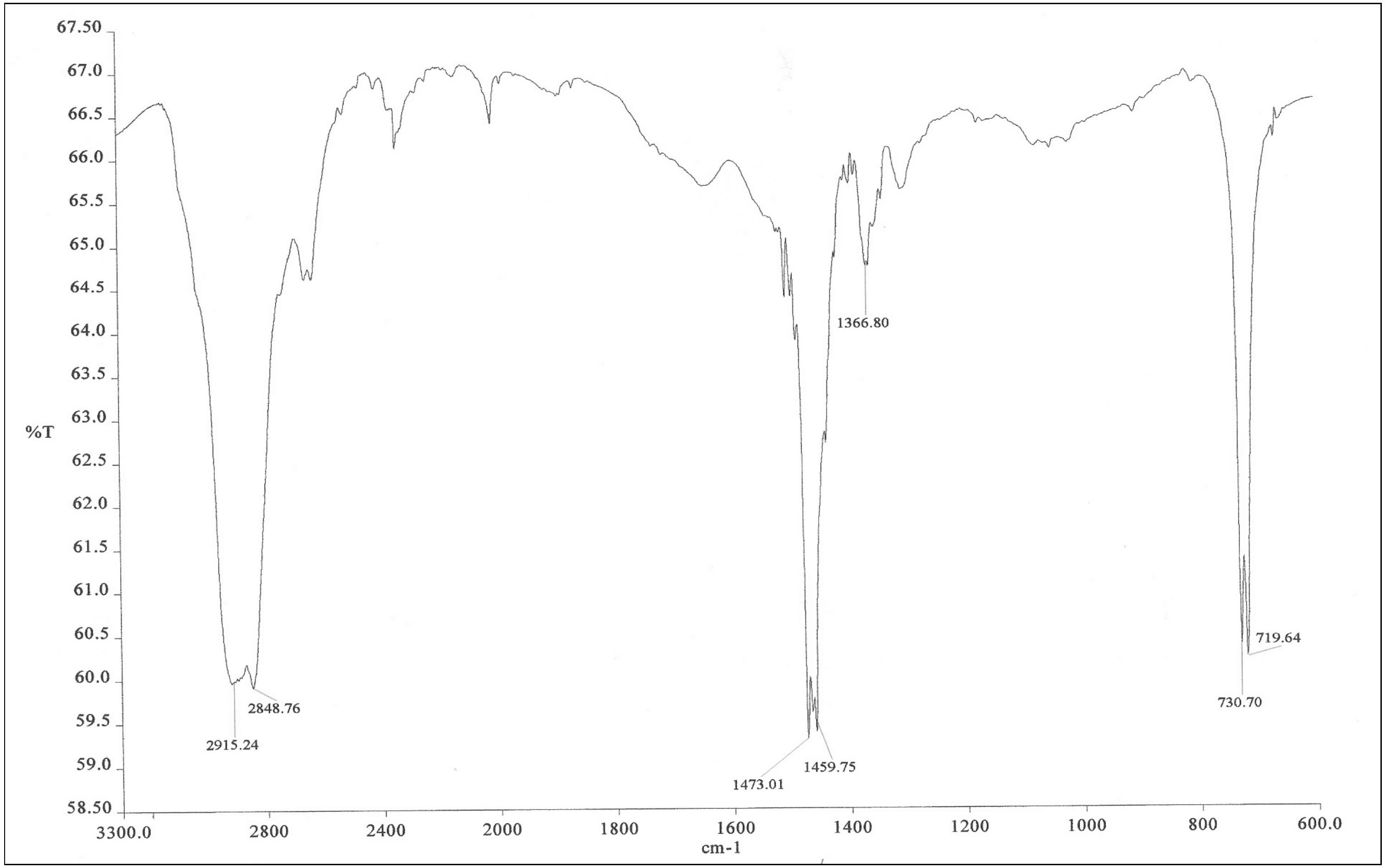


Figure 4.13: FT-IR spectrum of polyethylene obtained from $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 23.2

Strong bands in the 731-717 cm^{-1} region indicate the methylene rocking mode. It is known that absorption at 730 cm^{-1} is sensitive towards the crystalline fraction in the sample while the 720 cm^{-1} band arises from the amorphous section. The crystallinity content of polyethylene samples was determined by calculating the ratio of the absorbance at 730 and 720 cm^{-1}. Table 4.9 summarizes the absorption frequencies at 730 and 720 cm^{-1} for the IR spectra of polyethylene obtained from various Al/Cr molar ratios. All the PE samples showed absorption ratio around 1.00 reflects that the crystallinity of polyethylene produced was generally high. At Al/Cr ratio of 42.2, the absorption frequency at 730 cm^{-1} is more intense than the 720 cm^{-1}. This indicates that the polyethylene obtained from Al/Cr molar ratio of 42.2 was more crystalline compared with those obtained at lower Al/Cr molar ratio.

Table 4.9: A_{730}/A_{720} ratio for polyethylene obtained at various Al/Cr molar ratios

Al/Cr ratio	Intensity		Absorption ratio, A_{730}/A_{720}
	A_{730}	A_{720}	
23.2	0.0440	0.0449	0.98
30.8	0.0549	0.0568	0.97
31.2	0.0185	0.0189	0.98
40.0	0.0720	0.0731	0.98
42.2	0.0808	0.0774	1.04

Polymerization conditions:

Cocatalyst = $AlEt_2Cl$, gas temperature = 29°C, reactor temperature = 29°C,

aging time = 15 minutes, reaction time = 60 minutes,

volume = 2997 ml, solvent= toluene

(ii) Attenuated Total Reflection Infrared (ATR-IR) Spectroscopy

ATR spectroscopy enables samples to be examined directly in the solid or liquid state without pre-treatment[34]. It is an useful technique for analysis of materials and has become more popular nowadays.

Characterization test was carried out by placing the polyethylene samples prepared using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ catalyst on the Perkin-Elmer Spotlight 400 ATR-IR spectrometer. Spectra within the range of 650-4000 cm^{-1} were recorded and the absorption bands are shown in Table 4.10. ATR spectrum of polyethylene obtained at Al/Cr ratio 23.2 is presented in Figure 4.14. The spectra absorption bands were assigned and comparisons were made with spectra obtained by Fourier Transmission Infrared (FT-IR) spectroscopy.

The spectrum shows a strong absorption of CH_2 stretching in the range of 2915-2848 cm^{-1}. Band at 2915 cm^{-1} was due to asymmetric CH_2 stretching while 2848 cm^{-1} was assigned to symmetric CH_2 stretching. The CH_2 deformation band was found at 1472 cm^{-1}. Splitting of the band was observed.

Major characteristic peaks of polyethylene obtained by ATR spectroscopy were similar to FT-IR spectra. However, symmetric terminal CH_3 deformation band did not show up in ATR spectra. Besides, spectra obtained by attenuated total reflection infrared spectroscopy were ‘cleaner’ and did not contain spiky peaks. The absorption splitting was also sharper.

Table 4.10: ATR-IR band assignments of polyethylene at various Al/Cr molar ratios

Polyethylene vibration mode (cm^{-1})		Al/Cr ratio				
		23.2	30.8	31.2	40.0	42.2
CH$_2$- stretching	Asymmetric	2915 *s*	2914 *s*	2915 *s*	2915 *s*	2915 *s*
	Symmetric	2848 *s*	2848 *s*	2848 *s*	2848 *s*	2848 *s*
CH$_2$- deformation		1472 *m*	1472 *m*	1472 *m*	1472 *m*	1472 *m*
		1463 *m*	1463 *m*	1463 *m*	1463 *m*	1463 *m*
CH$_2$- rocking		730 *m*	731 *m*	730 *m*	730 *m*	730 *m*
		718 *m*	717 *m*	718 *m*	718 *m*	718 *m*

Abbrevations: *s* = strong; *m* = medium

CH$_2$ rocking mode appears at 730 cm^{-1} and 718 cm^{-1}. Absorbance ratio of these two peaks was calculated in order to determine the crystallinity of the sample. A summary of polyethylene absorbance ratio at different Al/Cr was shown in table 4.11. The overall ratio of A$_{730}$/A$_{720}$ was lower compared to ratio obtained by transmittance spectroscopy. All samples showed absorbance ratio around 0.50. The absorption frequency at 730 cm^{-1} is less intense than at 720 cm^{-1}. Polyethylene obtained from Al/Cr ratio 42.2 showed the highest value in absorbance ratio thus the degree of crystallinity is the highest among all polyethylene produced. As ATR technique analyses surface of the materials while the normal film sample analyses the internal part of samples, lower value in ATR absorbance ratio indicated the surface of polyethylene is less crystalline than the inner part of the samples. This may be due to part of the molecules which were purer and lower in density floated on top of other molecules thus causing the polyethylene surface more amorphous while for FT-IR technique, infrared radiation pass through more molecules therefore it showed the samples were more crystalline.

Table 4.11: A_{730}/A_{720} ratio for polyethylene at various Al/Cr molar ratios obtained by ATR technique

Al/Cr ratio	Intensity		A_{730}/A_{720}
	A_{730}	A_{720}	
23.19	0.0807	0.148	0.54
30.75	0.103	0.239	0.43
31.23	0.104	0.213	0.49
40.01	0.0951	0.175	0.54
42.15	0.109	0.190	0.57

Polymerization conditions:

Cocatalyst = $AlEt_2Cl$, gas temperature = 29°C, reactor temperature = 29°C,
aging time = 15 minutes, reaction time = 60 minutes,
volume = 2997 ml, solvent= toluene

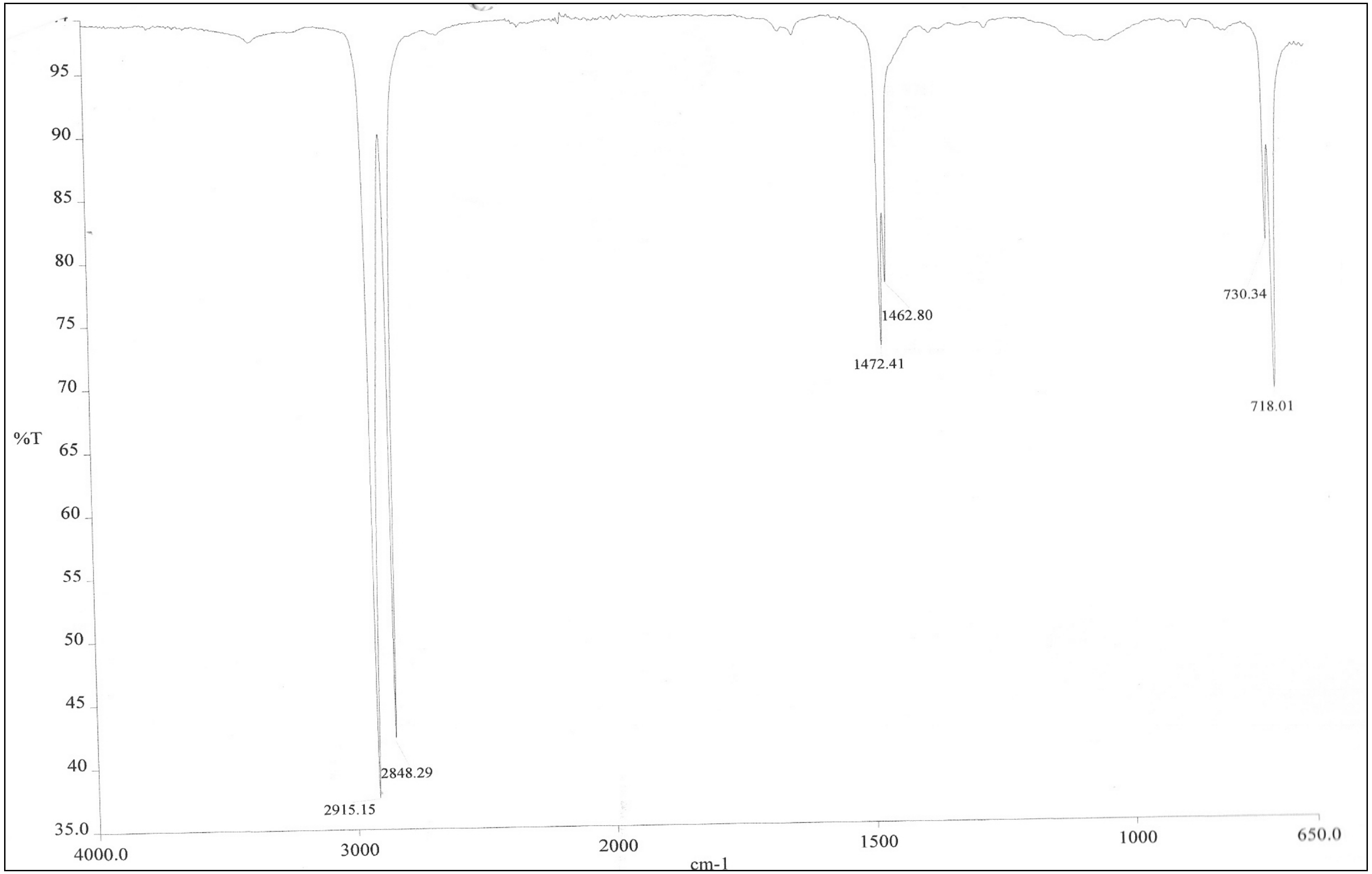


Figure 4.14: ATR spectrum of polyethylene obtained from $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 23.2

(b) Differential Scanning Calorimetri

DSC is often being used to measure a number of characteristic properties of a polymer sample such as melting point, glass transition temperature and crystallinity. The molecular weight of a polymer can be inferred from the DSC curve as polymers of lower grades would have lower melting points. Polymers prepared from heterogenous catalyst system would have different physical properties due to different chain length. In this study, DSC measurements were made on polyethylene prepared with $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ catalyst at Al/Cr molar ratio 23.2 to 42.2. Results obtained were listed in Table 4.12.

Table 4.12: DSC measurements of polyethylene at various Al/Cr molar ratios

Al/Cr ratio	First Heating			Cooling			Second Heating		
	T_m/ °C	T_o/ °C	ΔH/ J/g	T_c/ °C	T_o/ °C	- ΔH/ J/g	T_m/ °C	T_o/ °C	ΔH/ J/g
23.2	136	126	200	118	121	181	136	124	197
30.8	133	123	199	118	121	179	134	123	196
31.2	133	122	202	118	121	182	134	122	199
40.0	133	122	200	118	120	181	134	122	198
42.2	129	120	208	117	119	191	131	120	209

Polyethylene samples were analyzed as follow:

(i) Samples were heated from 35°C to 150°C at scanning rate 10°C/min.
(ii) After holding isothermally at 150°C for 10 minutes, the samples were cooled to initial temperature, 35°C at 5°C/min.
(iii) The samples were held 5 minutes at 35°C and were then heated again to 150°C at 10°C/min.

Figure 4.15, 4.16 and 4.17 illustrate the first heating, cooling and second heating curves of polyethylene at Al/Cr molar ratio 23.2. All the polyethylene samples display well defined endotherms with high melting temperature range between 129-136°C indicating the polyethylene samples are highly crystalline. The melting peaks increases slightly during second heating after annealing the samples at 35°C for 5 minutes. At higher $AlEt_2Cl$ concentration, lower melting temperatures were obtained. Decrease in melting point was observed as the Al/Cr increase implies a decrease in crystal perfection. T_m value for polyethylene sample at Al/Cr 42.2 was the smallest thus molecular weight of the sample may appear to be the lowest.

In the cooling scan, a sharp and well-defined crystallization peak with minimum temperature 118 °C was obtained. This indicated the ethylene units in the polymer chain were able to align and crystallize. The enthalpy of fusion reflects the amount of crystallinity in a polymer sample. The literature value for the enthalpy change of a single crystal of polyethylene is 293 J/g.[35] Enthalpy values obtained during second heating range from 199J/g to 208 J/g implied the polyethylene samples produced in this study were 68-71% crystalline. The ΔH value for polyethylene sample prepared at Al/Cr molar ratio 42.2 is the highest among all samples indicated the its crystallinity is the highest. This is in well agreement with A_{730}/A_{720} results obtained from infrared analysis.

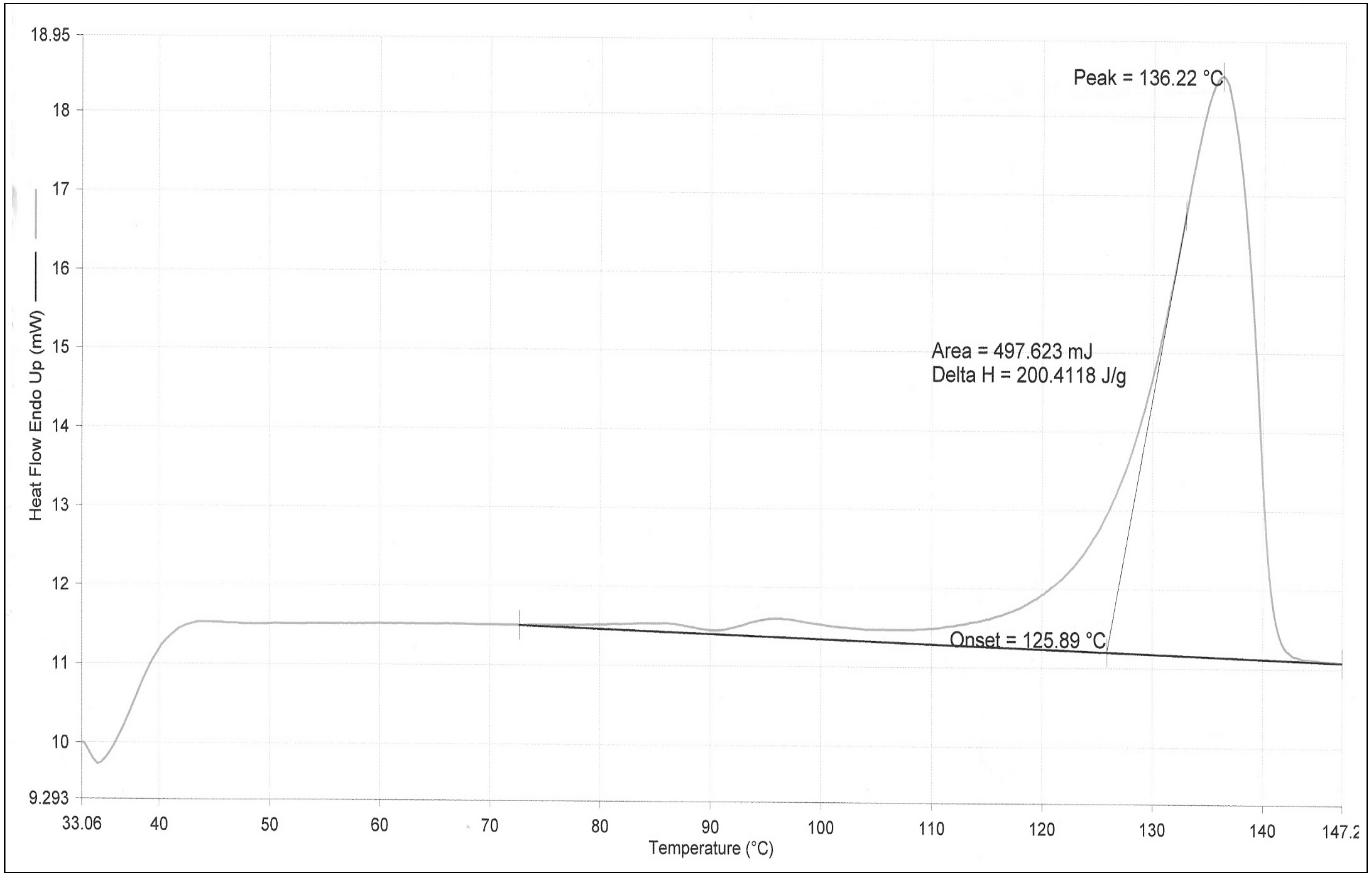


Figure 4.15: DSC first heating scan of polyethylene obtained from $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 23.2

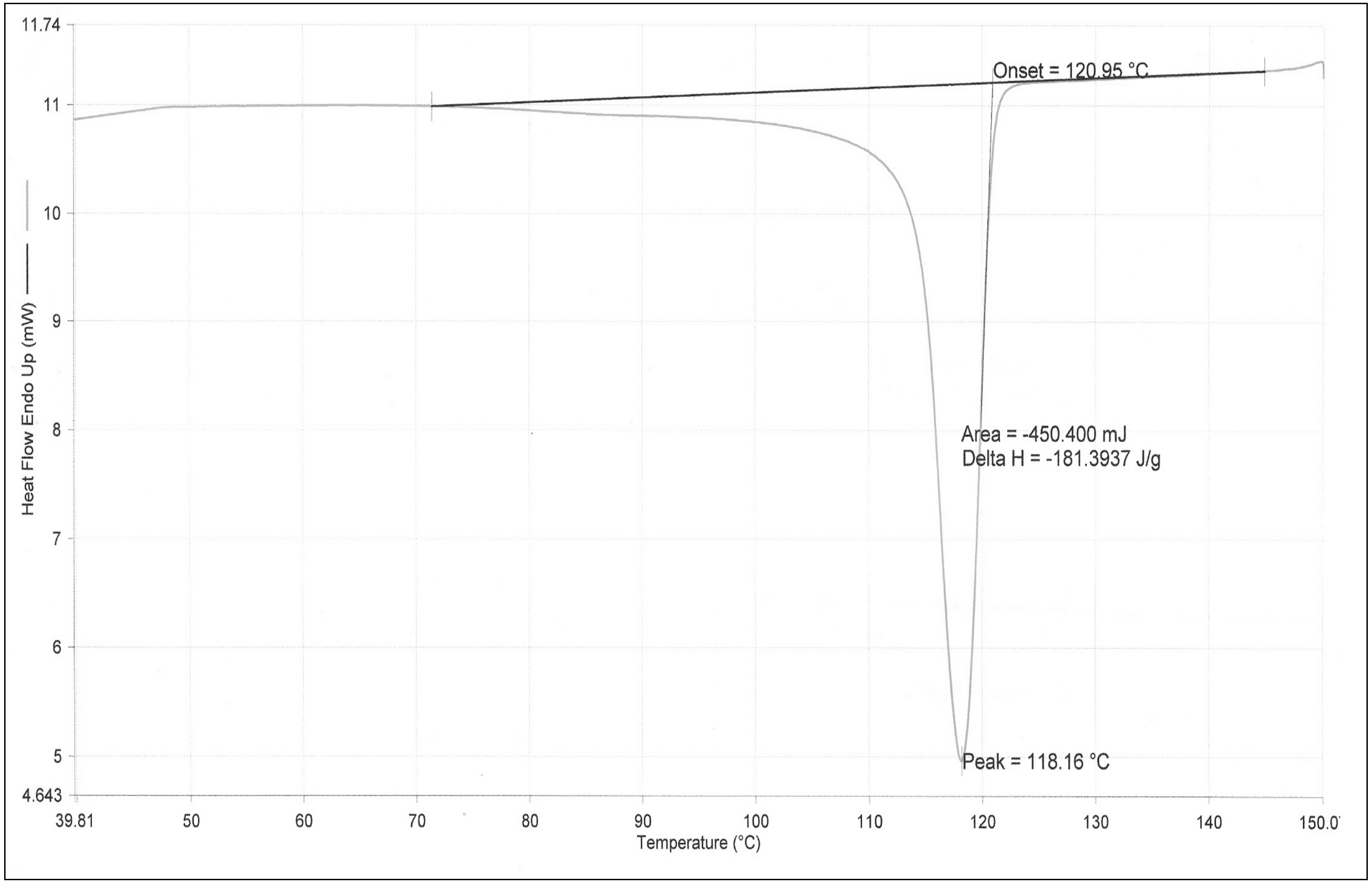


Figure 4.16: DSC cooling scan of polyethylene obtained from $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 23.2

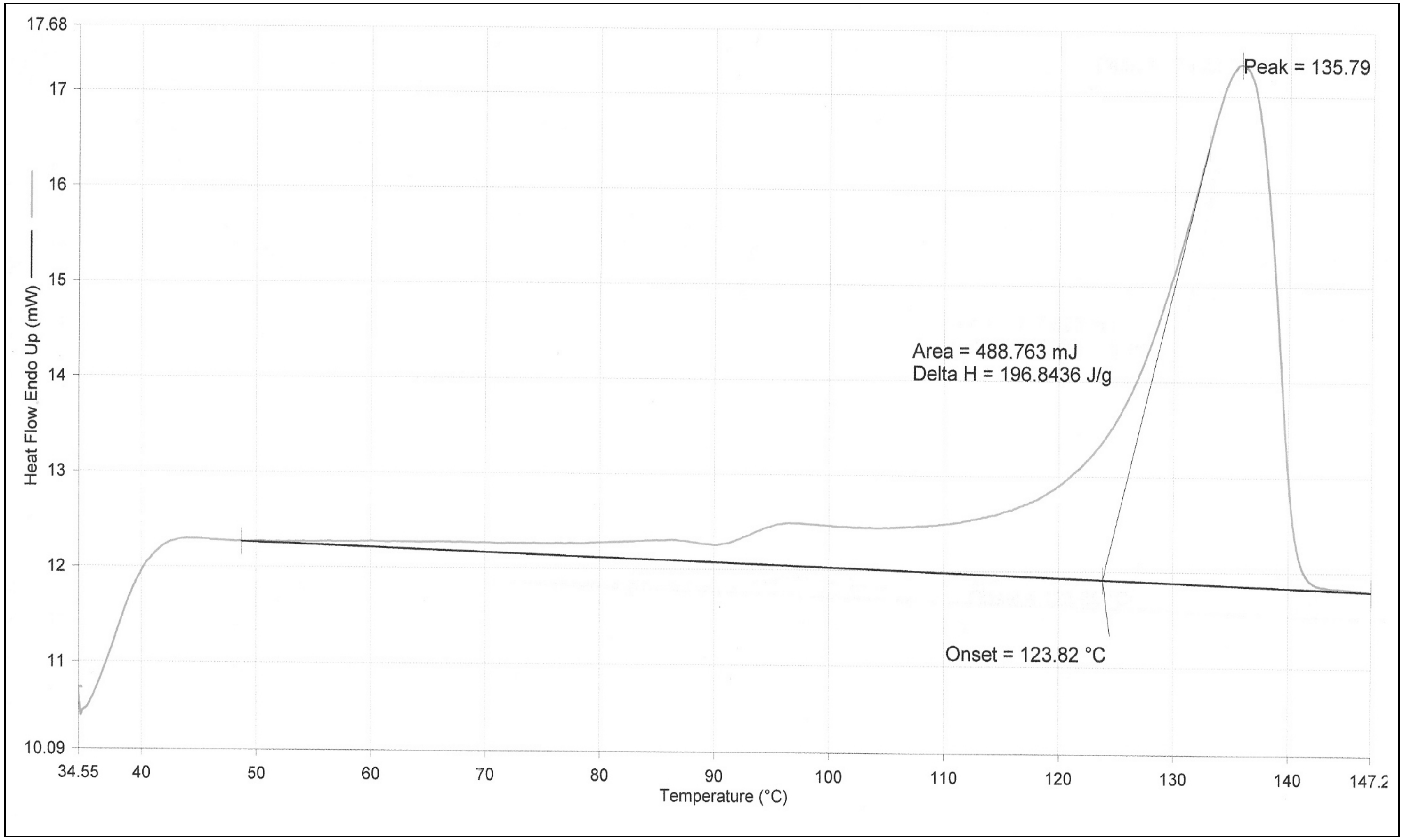


Figure 4.17: DSC second heating scan of polyethylene obtained from $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at Al/Cr molar ratio 23.2

4.9 Propylene Polymerization

Polymerization of propylene was carried out using the same constant volume set up as ethylene polymerization. Chromium(III) monochloroacetate complex, $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ was used as catalyst while the cocatalyst being diethylaluminium chloride.

Tap which connects the gas line and the reactor was opened when the polymerization gas line was filled with propylene monomer. Polymerization reaction carried out for one hour and the monomer gas pressure drop was noted. The activity was calculated from the pressure drop of monomer using Ideal Gas Law and was expressed as gPP/gCr/hr/atm.

After polymerization process, solution in the reactor was poured into 400 ml acidified methanol and stirred for a few hours. For most of the reactions, no or less significant product was found therefore filtration process could not be done. The solution was left to evaporate at room temperature to remove methanol and the product left behind was dried in the vacuum oven at 60°C for one day.

Attempts to produce polypropylene with $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ at room temperature were unsuccessful. The observed pressure drop was due to the amount of monomer required to saturate the toluene solvent but not to form product. At Al/Cr 59.2, some fine droplets were found on the wall of the reactor. Upon precipitation in acidified methanol, a thin layer of oily product with yellowish colour and bad smell was formed. No solid product was observed.

Polymerization runs were continued to carry out at temperatures around 0-4°C. The reactor was put in an ice-bath and the Al/Cr was maintained at 59. Oily product formed after quenching and stirring process for most of the runs were too little. Only the product obtained from polymerization reaction at temperature 3°C and Al/Cr 59.7 was able to be characterized by FT-IR and DSC.

FT-IR spectrum obtained was compared with the published results of polypropylene.[36-38] Table 4.13 summarized the FT-IR band assignments of the analyzed sample. The FT-IR spectrum showed some characteristic peaks of isotactic polypropylene. The bands at 2870 and 2957 cm^{-1} are assigned to CH_3 stretching modes. The bands at 2849 and 2917 cm^{-1} correspond to symmetric and asymmetric stretching of CH_2 respectively. CH_2 deformation mode appears at 1462 cm^{-1} while absorption at 1377 cm^{-1} is due to symmetric deformation of terminal CH_3.

CH_2 twisting and CH bending mode give rise to absorption peak at 1261 cm^{-1}. Infrared absorption at 1150 and 1020 cm-1 are assigned as C-CH_3 stretching. CH_2 rocking mode, C-CH_3 stretching and equatorial C-C bond stretching occur at 803 cm^{-1}.[39-40]

DSC heating curve of the sample showed a broad endotherm with melting temperature 143°C which is lower than polypropylene homopolymer (160°C). Lower melting point and the oily product obtained after polymerization reaction may suggest that the product was not 100% polypropylene. The drop in monomer pressure during the reaction might be due to the formation of oligomers. DSC thermogram for the sample was shown in Figure 4.18.

Table 4.13: IR analysis of the product obtained for propylene polymerization at temperature 3°C and Al/Cr molar ratio 59.7

Vibration mode		IR band (cm^{-1})
CH_3- stretching		2957 2870
CH_2- stretching	Asymmetric	2917
	Symmetric	2849
CH_2 deformation		1462
Symmetric terminal CH_3 deformation		1377
CH_2 twisting CH bending		1261
C-CH_3 stretching		1150 1020
CH_2 rocking equatorial C-C stretching		803

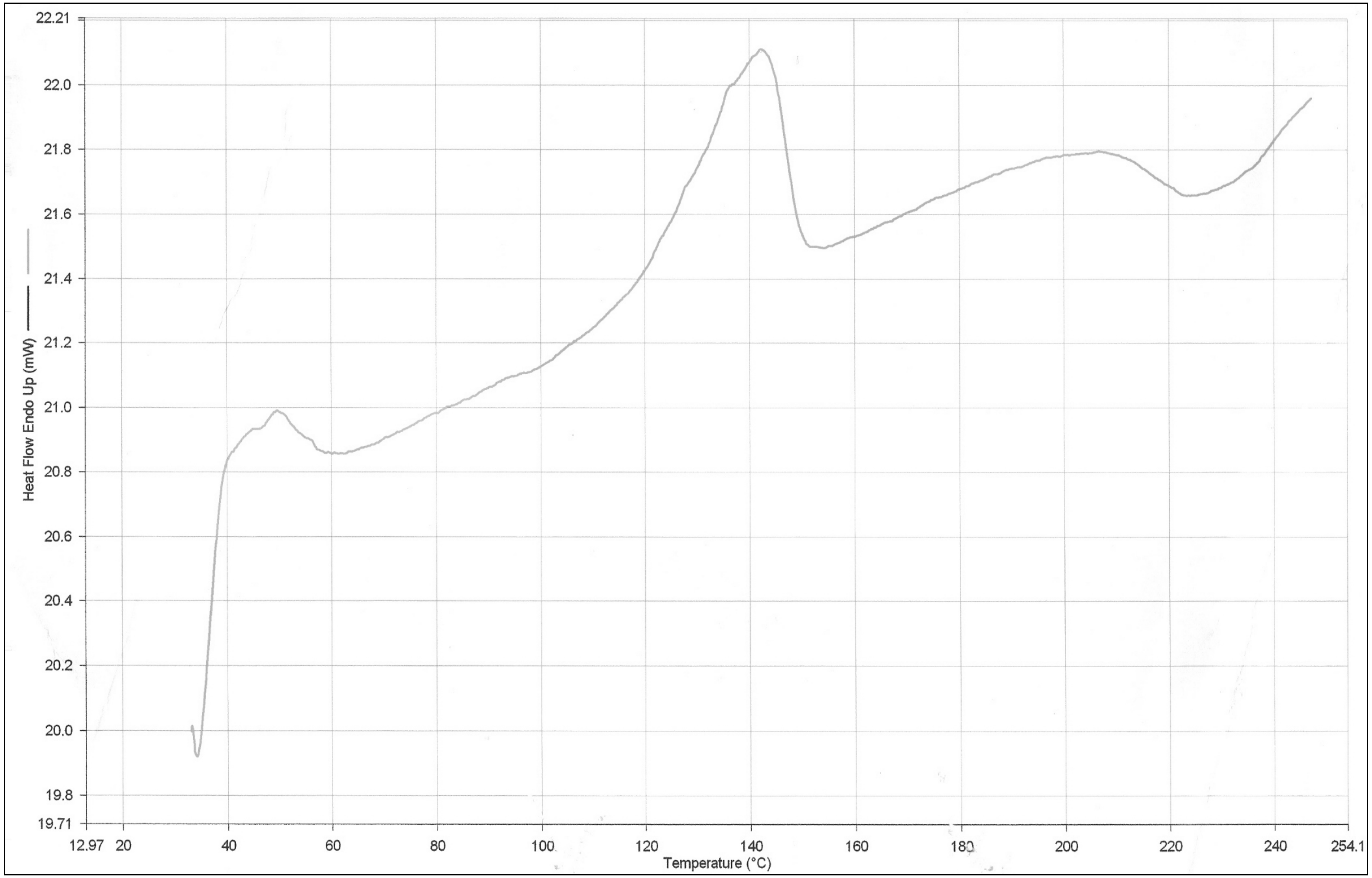


Figure 4.18: DSC thermogram of sample obtained from polymerization of propylene at Al/Cr molar ratio 50.7 and temperature 3°C

The heterogenous catalyst system in this study showed very little activity for propylene. Similar observation was found by Soga et al.[1] in the homo-polymerization of propylene with $Cr(C_{17}H_{35}COO)_3/AlEt_2Cl$ catalystic system in toluene. Incapable of propylene polymerization might be attributed to the formulation of a stable complex (eg. π-allyl) between the Cr^{2+} species and propylene during the reaction. According to Haward et al.[41], catalysts active for ethylene polymerization usually showed little activity for propylene polymerization. Therefore, magnesium chloride-supported catalysts have been use by many researchers for the polymerization of propylene.[1,42-45]

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