CHAPTER 5

RESULTS AND DISCUSSION:

ETHYLENE AND PROPYLENE COPOLYMERIZATION USING $[Cr_3(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ AS ZIEGLER-NATTA CATALYST

5.1 Copolymerization of Ethylene with Propylene

Linear low density polyethylene (LLDPE) has gained much attention in industry. Copolymerization of ethylene with α-olefins leads to the formation of linear low density polyethylene. The desirable properties of copolymers such as flexibility, impact strength and transparency made them become one of the most important commercial products worldwide. Copolymerization of ethylene with a smaller amount of propylene results in amorphous rubbery materials. Blends of amorphous ethylene-propylene copolymers with isotactic polypropylene are widely used as impact strength modifiers.[1-2]

Soga and coworkers[3] copolymerized ethylene and propylene using a soluble chromium catalytic system composed of $Cr(C_{17}H_{35}COO)_3$ and $AlEt_2Cl$. The catalytic system produced random copolymer with a narrow molecular weight distribution. A few years later, Gan et al.[4] successfully produced ethylene-propylene copolymer with $Cr(CH_3COO)_3/AlEt_2Cl$ catalyst system.

Chromium(III)monochloroacetate catalyst, $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ used in this study shows high activity in ethylene polymerization but it is incapable to produce polypropylene. Following this, ethylene monomer was copolymerized with propylene and the results show that $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ can copolymerize ethylene and propylene to produce random copolymers.

Copolymerization of ethylene and propylene was carried out in a 250 ml reaction flask connected to the gas line. The ethylene and propylene monomers were allowed to mix for 1 hour. Chromium(III) monochloroacetate and diethylaluminium chloride catalyst system was left to 'age' for 1 hour before the reaction starts. Copolymerization was performed for one hour. The average activity was calculated from total yield of copolymer formed divided by the weight of Cr in the catalyst and was expressed as grams of copolymer per gram of Cr per hour.

5.2 Effect of Different Ethylene-Propylene Content

Ethylene-propylene copolymers were prepared at room temperature using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system. 0.02g catalyst was used and the Al/Cr was 30.8. Toluene was used as solvent in the reaction. A series of copolymerization reactions were carried out at various ethylene-propylene monomer ratio. It was assumed that both ethylene and propylene behave like perfect gases.[5]

Throughout the reactions, the catalyst and products remained as fine dispersion in the solution. Fine white powdery product formed after the copolymer was precipitated with acidified methanol. As the propylene content in the monomer mixture increases, the product yield decreases. No solid product was formed when the mol % of propylene in monomer mixture was as high as 90%. Light yellowish oily droplets with bad smell formed on the surface of the solution. Table 5.1 summarized the catalytic activity and copolymer yield obtained at different ethylene-propylene content.

Table 5.1: Copolymer yield produced at different ethylene and propylene content

% E	**% P**	**Al/Cr**	**Yield g**	**Average activity (g copolymer per g Cr per h)**
100.0	0.0	30.8	0.315	92.8
89.7	10.3	30.8	0.214	60.8
79.8	20.3	30.3	0.197	57.0
69.9	30.1	30.8	0.170	48.3
59.8	40.2	30.9	0.127	37.7
50.1	49.9	30.8	0.0938	27.6
39.9	60.1	30.3	0.0497	14.4
30.4	69.6	30.9	0.0495	14.4
20.1	79.9	30.6	0.0490	14.3
10.3	89.7	30.6	-	-
0.0	100.0	30.8	-	-

Copolymerization conditions:

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

temperature= 30°C, aging time = 60 minutes

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

Results from Table 5.1 showed that maximum average activity was attained when ethylene monomer content was the highest. The average activity was as high as 60.8 g copolymer/g Cr/ hr at 89.7% of ethylene content. The catalytic activity dropped as the amount of ethylene in the mixture decreases.

Typical kinetic curves of ethylene-propylene copolymerization were shown in Figure 5.1 and Figure 5.2. The curves are of decay-type. The catalytic activity increases to a maximum and then decreases sharply to a steady state. Copolymerization took place when the monomers diffused into toluene solvent and reached the catalyst active centers. The decrease of activity with time was due to the instability of active centres caused by structural changes. Similar observation has been made by Gan et al.[4] on copolymerization of ethylene and propylene using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system.

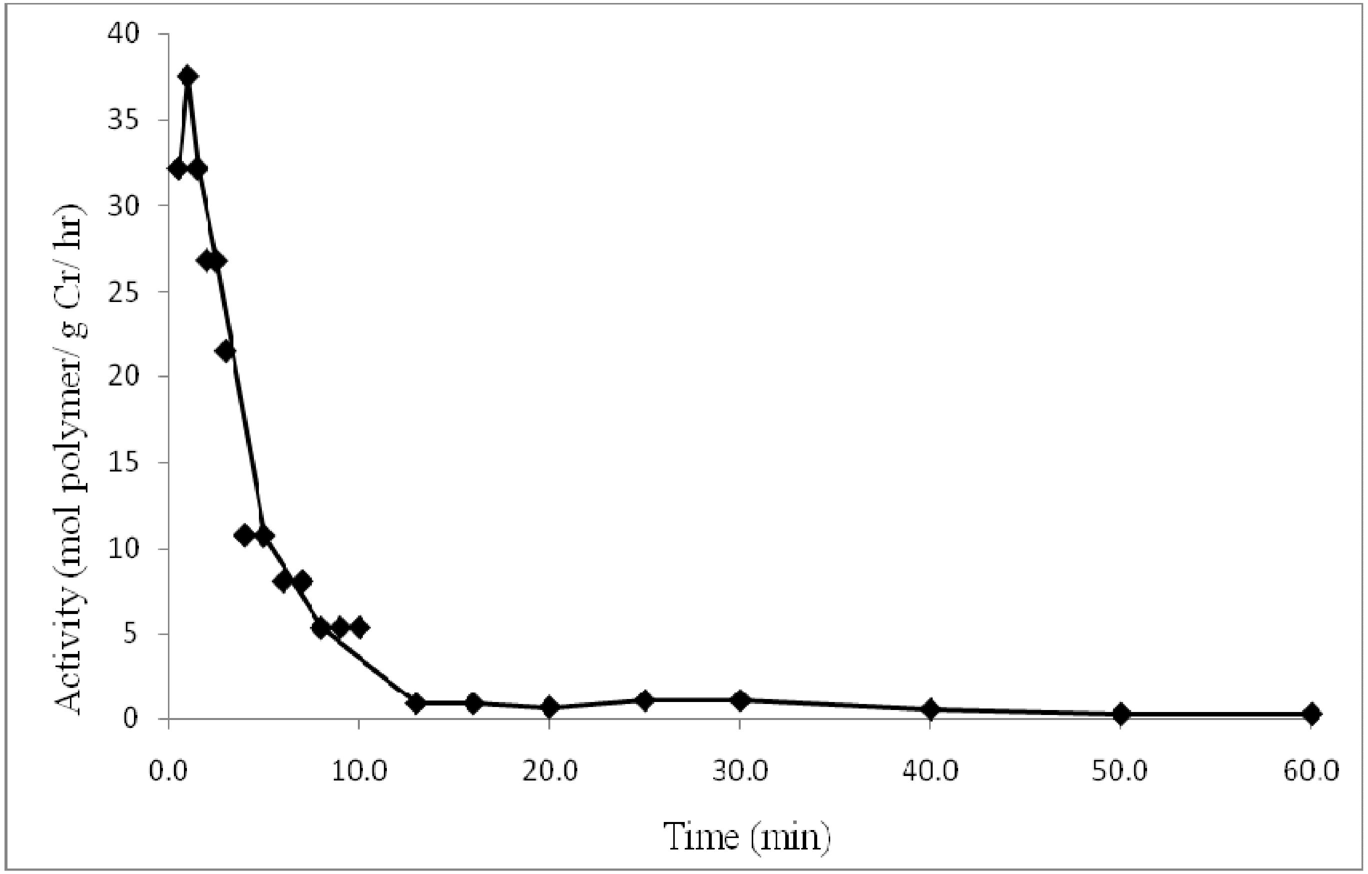


Figure 5.1: Kinetic curve of ethylene-propylene copolymerization with $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system; monomer mixture: Ethylene 89.7 %, Propylene 10.3 %

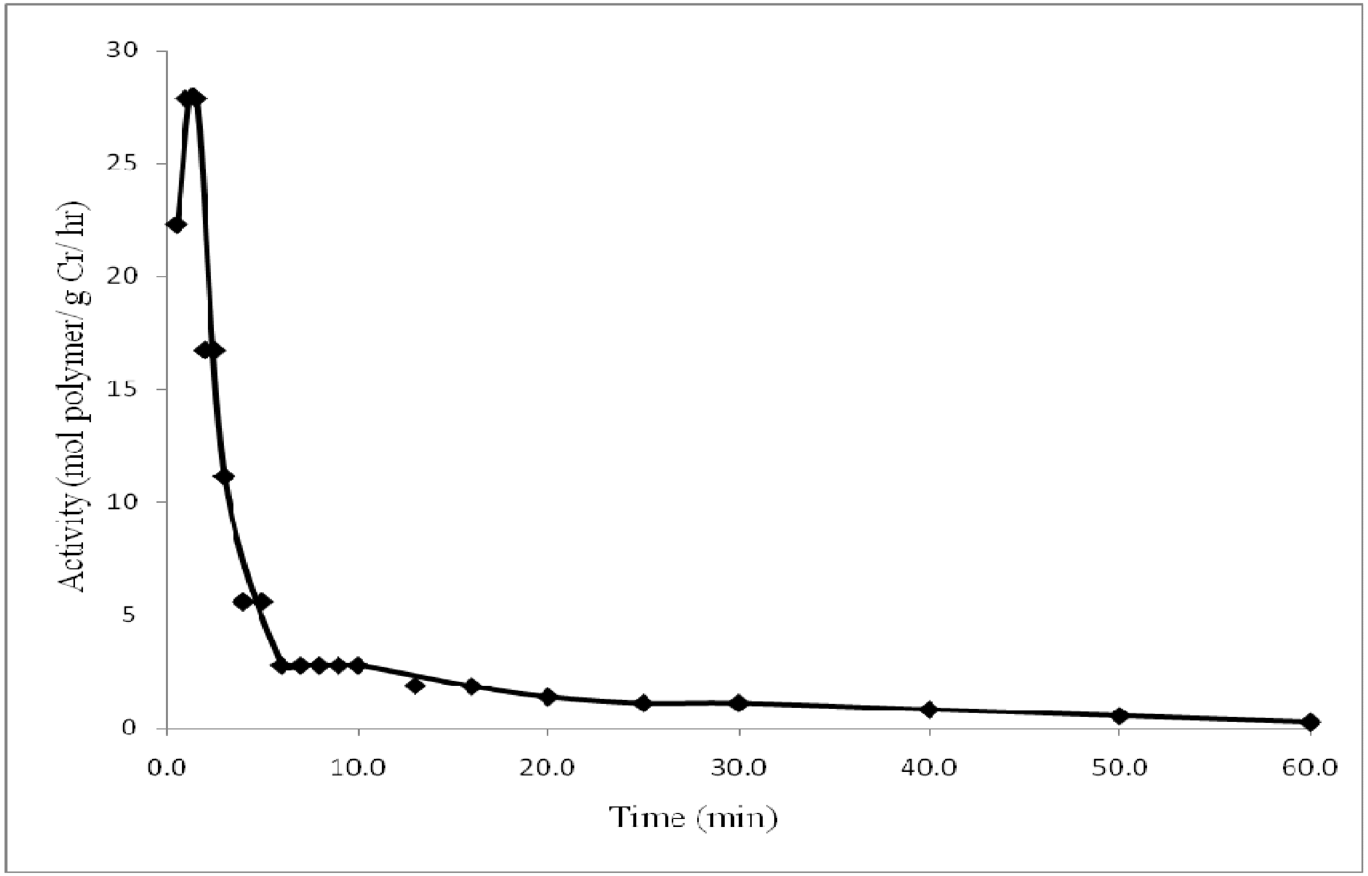


Figure 5.2: Kinetic curve of ethylene-propylene copolymerization with $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system; monomer mixture: Ethylene 50.1 %, Propylene 49.9 %

5.3 Effect of Catalyst and Cocatalyst Aging Time

Aging time of catalyst is one of the variables that influence the kinetic of the reaction. It has been shown that the oxidation state of Cr in the active catalyst is II[3,6], sufficient pre-reaction time or 'aging' time is required for the catalyst and cocatalyst to react and reduce the oxidation state of Cr from Cr^{3+} to Cr^{2+}.

In this study, diethylaluminium chloride was used as cocatalyst. It acts as a chain transfer agent[7] and formed a complex with Cr(III) monochloroacetate catalyst to make it ready for polymerization. A number of polymerization runs were carried out at room temperature to study the polymerization activity affected by the aging time between catalyst and cocatalyst. Mixture of catalyst and cocatalyst was allowed to react from 15 minutes to 180 minutes before introducing the monomer mixture. Al/Cr molar ratio was set constant at 30.8 while the mol % of ethylene to mol % propylene was maintained at 50:50. Results obtained were shown in Table 5.2.

Table 5.2: Effect of aging time between catalyst and cocatalyst

Aging time/ min	% E	% P	Yield g
15	49.9	50.1	0.0337
30	50.0	50.0	0.0891
60	50.1	49.9	0.0938
120	50.1	49.9	0.1218
180	50.1	49.9	0.0739
240	49.9	50.1	0.0398

Copolymerization conditions:

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

Al/Cr = 30.8, temperature= 30°C, reaction time = 60 minutes,

volume = 2997 ml, solvent= toluene

All the copolymerization reactions were terminated after 60 minutes and the white powdery products were quenched with methanol and hydrochloric acid. When the aging time between the catalyst and cocatalyst is less than 30 minutes, less colour change was observed as compared to the changes occurred for longer aging time. This can be explained as the co-catalyst and the catalyst had not fully reacted. Not many active sites were formed therefore caused incompleteness of the copolymerization reaction.

Optimum activity was reached if the catalyst and cocatalyst reacted 30 minutes to 2 hours before copolymerization reaction started. The colour of the mixture gradually changed from green to pale yellow and later on to light orange indicated the reduction of Cr^{3+} to Cr^{2+}. Prolonged aging time leads to a drop in activity. Similar trend was observed in the copolymerization of ethylene and propylene using chromium(III) actate and diethylaluminium chloride by Gan and coworkers[4].

The kinetic behavior of the catalyst for different aging time was illustrated in Figure 5.3. The catalytic activity increases sharply to a maximum within a short period of time and drops to a steady state. The decrease in activity might be due to to the viscosity of the polymerization medium increases as the run proceeds. As the copolymerization reaction goes on, the amount of insoluble product formed in the mixture increases. The active centre was being encapsulated by the copolymer thus the diffusion of monomer to reach the active centre is more difficult and caused a drop in the copolymerization rate. Kinetic curve of aging time 15 minutes showed that the catalyst system was only active for copolymerization for a short period. The catalytic activity terminated after 30 minutes and no further drop in monomer pressure was observed.

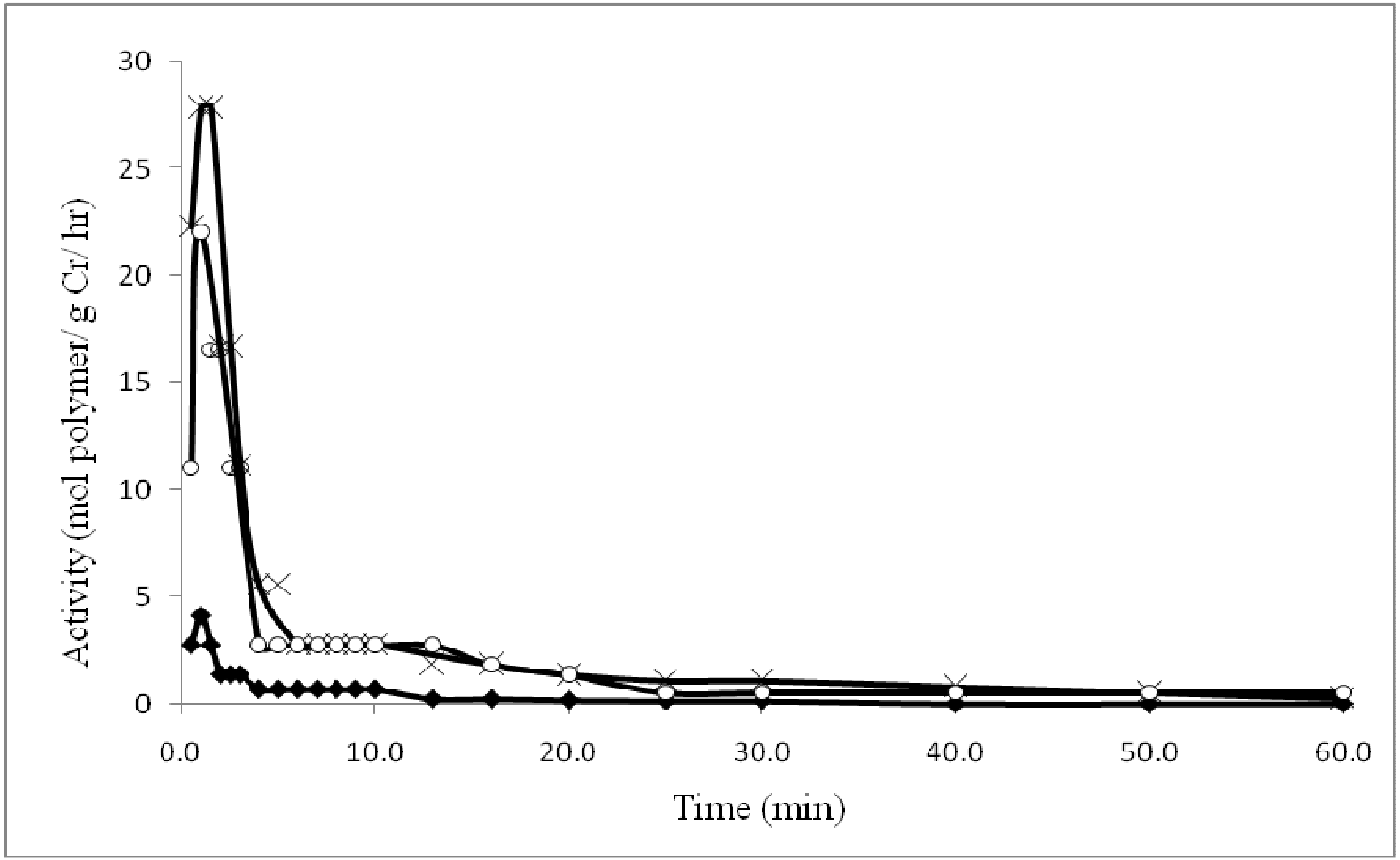


Figure 5.3: Kinetic curves for ethylene-propylene copolymerization using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system at different aging time:◆ , 15 minutes; x, 60 minutes; ○ , 180 minutes

5.4 Effect of Al/Cr Ratio

In all Ziegler-Natta polymerizations, the molar ratio of the organometallic cocatalyst to the transition metal catalyst can affect the product yield, the polymerization rate, the degree of stereoregularity and the molecular weight of the resulting polymer. Many studies have shown the influence of the ratio of cocatalyst to catalyst on polymerization.[8-10]

The effect of the Al/Cr molar ratio on the copolymerization activity was studied. Ethylene-propylene copolymerization runs were carried out at different Al/Cr ratios ranging from 20.0 to 38.6. $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system was used in all the experiments. The amount of chromium complex used was set constant at 0.02g while the amount of diethylaluminium was varied. Ethylen-propylene content was mantained at around 50%-50%.The reactions were carried out at room temperature. Dependence of the catalytic activity on the Al/Cr ratio was summarized in Table 5.3.

Results showed that the aluminium alkyl strongly affects the copolymerization yield. The activity reaches maximum at Al/Cr ratio 30.8 where 27.6g copolymer/g Cr/hr is attained. Lowering in copolymer yield and average activity was observed if the Al/Cr molar ratio is less than 30.8. On the other hand, Al/Cr ratio higher than 30.8 tends to decrease the average rate of the copolymerization reaction. Figure 5.4 showed the dependence of average catalytic activity on different Al/Cr molar ratio.

Table 5.3: Effect of Al/Cr molar ratio on copolymer yield and average activity

Al/Cr ratio	%E	%P	Yield/ g	Average activity/ g copolymer per g Cr per hr
20.0	50.0	50.0	0.0219	6.4
24.6	50.1	49.9	0.0507	14.8
30.8	50.0	50.0	0.0938	27.6
34.3	49.9	50.1	0.0863	26.3
38.6	50.0	50.0	0.0399	11.6

Copolymerization conditions:

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

temperature= 30°C, aging time = 60 minutes, reaction time = 60 minutes,

volume = 2997 ml, solvent= toluene

.

Bohm[11] explained this tendency in terms of a competition of the monomer and the aluminium alkyl for the same active sites of the catalyst. Besides, at a high concentration of $AlEt_2Cl$, overreduction of Cr^{3+} to Cr^{+} and Cr^{0} might occur, the species are not active for copolymerization of ethylene and propylene.[12-13] The decrease in activity when the Al/Cr is higher than the optimum ratio might also be attributed to inhibition of catalyst active centres by the diethylaluminium cocatalyst. the nature of the catalyst[14] and the valency of the transition metal[15] change with the ratio of the catalyst components.

Figure 5.5 shows the plots of maximum initial activity versus time for copolymerization runs at different Al/Cr molar ratios. A short induction period was observed whereby the activity rose rapidly to a maximum followed by a decay period when the activity decreased to a stationary state.

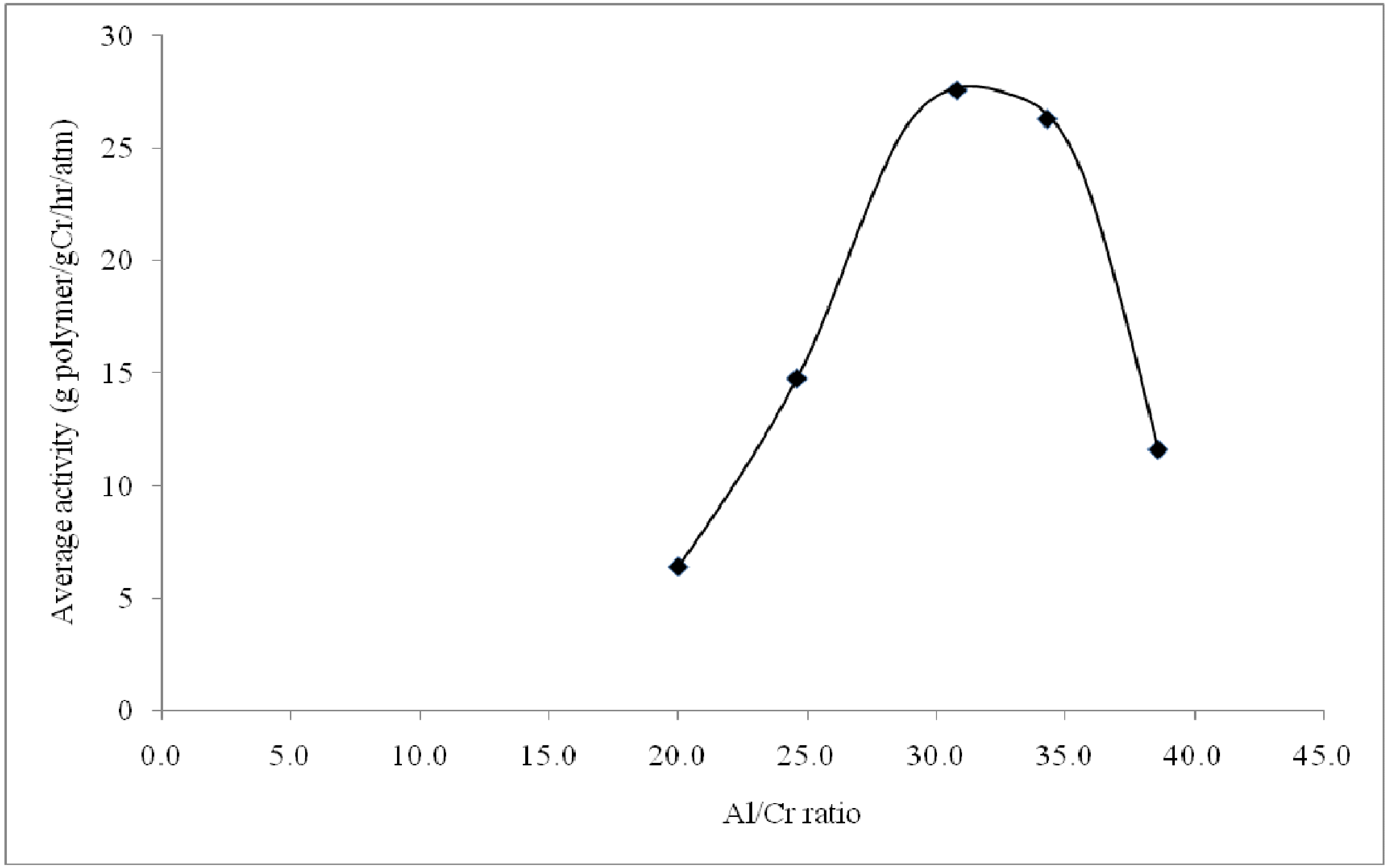


Figure 5.4: Effect of varying Al/Cr molar ratio on the average activity of ethylene-propylene copolymerization.

Catalyst system= $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$, temperature= 30°C,

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

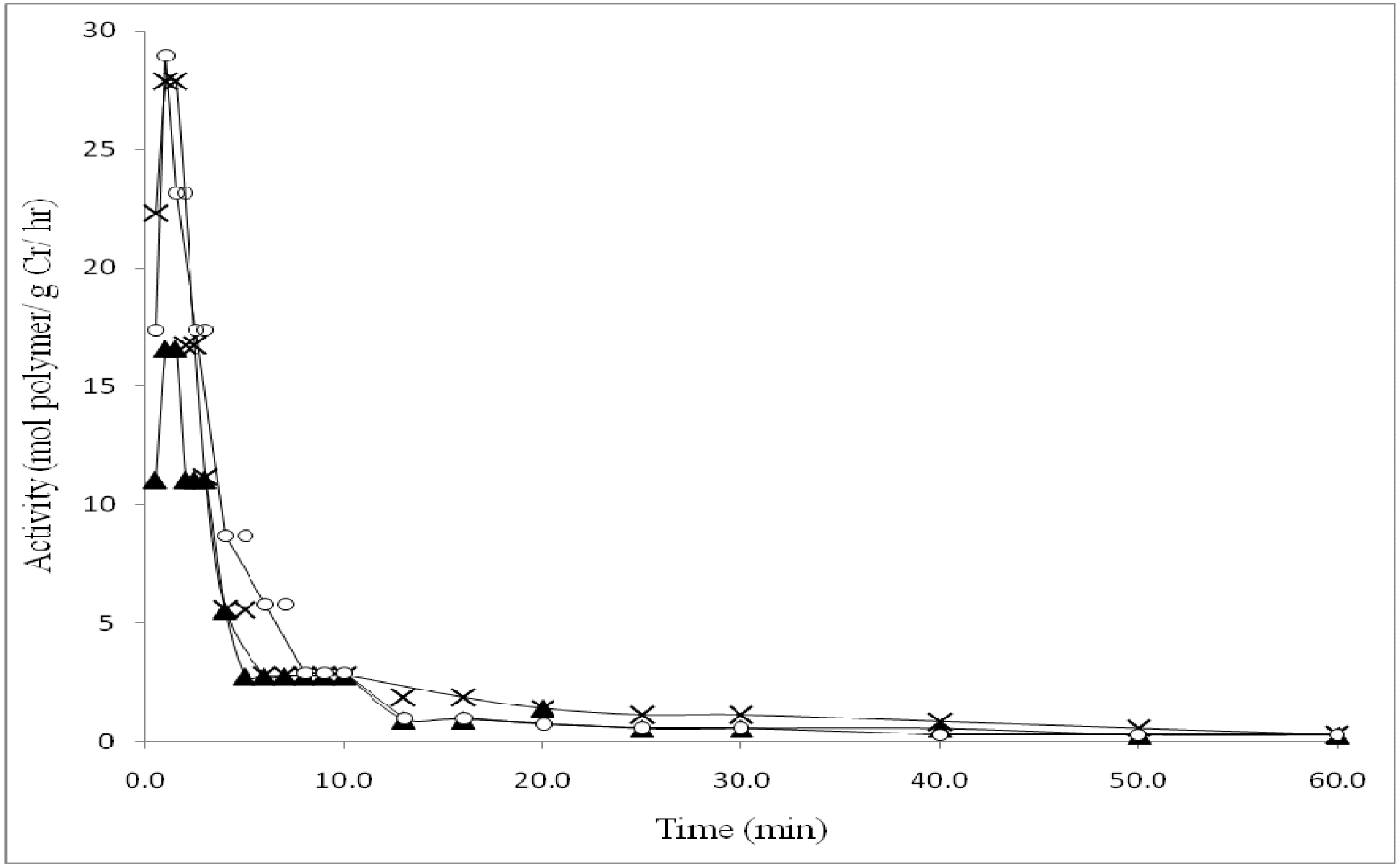


Figure 5.5: Kinetic curves of ethylene-propylene copolymerization with

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

at different Al/Cr molar ratios: ▲, Al/Cr= 24.6; x, Al/Cr= 30.8; ○, Al/Cr= 34.3

5.5 Characterization of Copolymer

(a) Infrared Spectroscopy

Polymers prepared by Ziegler-Natta copolymerization of ethylene and propylene have a wide range of commercial and practical applications[16-17]. Therefore, determination of the distribution of the two monomeric units along the copolymer chain is important in the study of copolymerization in order to produce E-P copolymers with good quality.

Two different methods have been reported by Natta and coworkers in the determination of ethylene–propylene copolymer compositions.[18] One is a radiochemical method, where ethylene containing radioactive C^{14} was copolymerized with propylene, and the E-P composition was estimated by radioactivity counting of the copolymer. The other method involves the measurement of infrared absorption at 719cm^{-1} of the copolymer in CCl_4 solutions. The results obtained by the two methods were quite satisfactory. However, these methods were time consuming.

One of the most widely used method to characterize ethylene-propylene copolymers is infrared spectroscopy.[19-20] Wei[21] and Gőssl[22] described a simple and rapid method to determine the ethylene-propylene composition in a copolymer. IR analysis was made on solid copolymer films and this avoids the solution problems. The ratio of the absorption at two selected peaks is directly proportional to the ratio of ethylene and propylene units in the copolymer.

Polyethylene has characteristic infrared absorption peaks at 1463, 1376 and 720 cm^{-1}. Absorption at 720 cm^{-1} represents the block methylene rocking vibration. As the copolymer propylene content increases, the sequence length of methylene units in the block decreases.[20]

Table 5.4: IR band assignments for ethylene-propylene copolymers

% E	% P	Bands arise from polyethylene (cm^{-1})			Bands arise from polypropylene (cm^{-1})		
		CH_3-deformation	CH_2- deformation	CH_2 rocking	CH_2 twisting and CH bending	C-CH_3 stretching	CH_2- rocking, C-CH_3 stretching and C-C stretching
100.0	0.0	1463	1369	720, 731	-	-	-
89.7	10.3	1464	1376	719	1259		802
79.8	20.2	1463	1377	720, 730	1261	1020	801
69.9	30.1	1463	1377	720, 730	1262	1023	803
59.9	40.1	1462	1378	720, 730	1262	1024	804
50.1	49.9	1463	1378	720, 730	1262	1022	803
39.9	60.1	1463	1378	720, 730	1262	1022	803
30.4	69.6	1463	1378	720, 730	1262	1023	804
20.1	79.9	1463	1378	720, 730	1262	1023	806

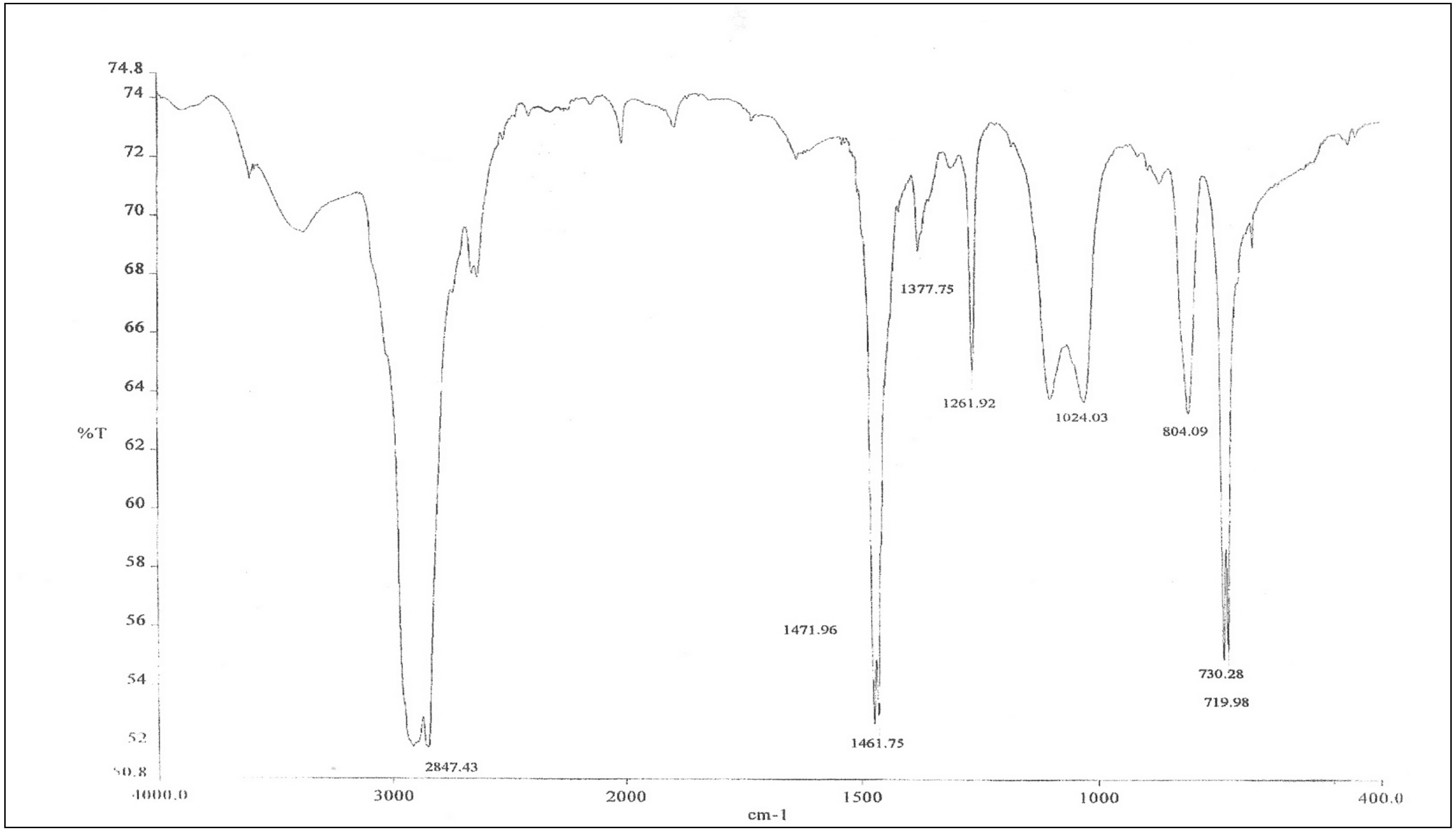


Figure 5.6: Infrared spectrum of ethylene-propylene copolymer obtained using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system at temperature= 30°C, aging time = 60 minutes, reaction time = 60 minutes, volume = 2997 ml, solvent= toluene

Splitting of CH_2 rocking into two bands at 720 and 730 cm^{-1} was observed in all spectra. This showed that copolymers prepared by $Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O/AlEt_2Cl$ catalyst system have substantial polyethylene crystallinity. Absorption band at 1376 cm^{-1} has been assigned to symmetric CH_3 deformation while band at 1463 cm^{-1} is due to CH_2 deformation mode.

Polypropylene gives rise to infrared absorption peaks at 968 cm^{-1} and 1150 cm^{-1} which correspond to methyl rocking and methyl wagging respectively. However, these two bands appear weak or missing in all spectra. According to Drushel and Iddings,[23] the catalyst used and physical properties of the copolymer affect the intensity of both 968 cm^{-1} and 1150 cm^{-1} band. As copolymerization became more random, more 'isolated' propylene units were yielded and the two bands became less intense and more diffuse. Infrared absorption at 1260 cm^{-1} is due to CH_2 twisting mode and CH bending. C-CH_3 bond stretching of isotactic polypropylene occurs at 1024 cm^{-1} while absorption peak around 804 cm^{-1} corresponds to CH_2 rocking mode, C-CH_3 stretching and equatorial C-C bond stretching.[24-25] From the infrared absorption results, it can be suggested that the ethylene-propylene copolymers produced in this study are of isotactic type. Infrared band assignments of ethylene-propylene copolymers produced with different mol % monomer were listed in Table 5.4. Figure 5.6 shows the infrared spectrum for ethylene-propylene copolymer produced. Infrared spectra with almost similar absorption peaks were obtained by Wei.[21]

A number of IR band ratios have been utilized in the determination of ethylene-propylene copolymers. Band ratios of A_{720}/A_{1376} and A_{1376}/A_{1463} were investigated in this study for possible application in the analysis of E-P copolymer. As shown in Figure 5.7, base lines were drawn for the chosen IR peaks to determine the peak height. Ratio of the peak height between the two peaks was then calculated. Table 5.5 summarized A_{720}/A_{1376} and A_{1376}/A_{1463} peaks ratio.

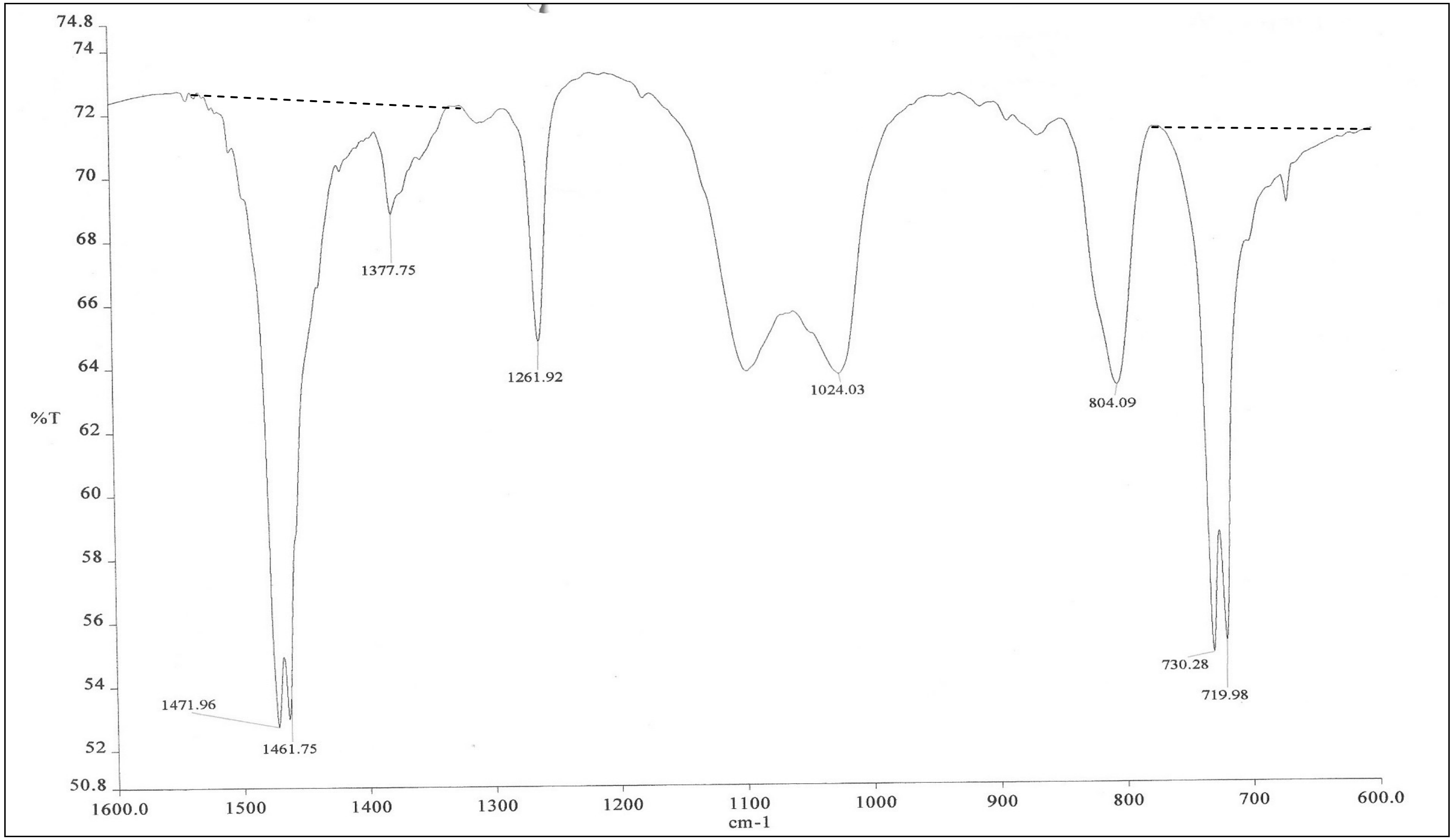


Figure 5.7: FT-IR spectrum of E-P copolymer in the range of 1600-600cm^{-1}.

Baseline used for measurement of A_{720}, A_{1376} and A_{1463}

Table 5.5: IR analysis of ethylene-propylene copolymer

% E	% P	Peaks ratio	
		A_{720}/A_{1376}	A_{1376}/A_{1463}
100.0	0.0	13.1	0.070
89.7	10.3	3.57	0.129
79.8	20.2	3.46	0.147
69.9	30.1	3.20	0.183
59.9	40.1	2.88	0.232
50.1	49.9	2.44	0.338
39.9	60.1	2.29	0.348
30.4	69.6	2.23	0.350
20.1	79.9	1.98	0.379

The obtained results showed that A_{720}/A_{1376} decreases as the mol % of propylene increases while A_{1376}/A_{1463} ratio rises from 0.070 to 0.379 when the mol % of propylene increases from 0.0% to 79.9%. The absorbance ratios of the ethylene-propylene copolymers were illustrated in Figure 5.8 and Figure 5.9. Both absorbance ratios showed almost linear relationship when they were plotted against mol % of ethylene.

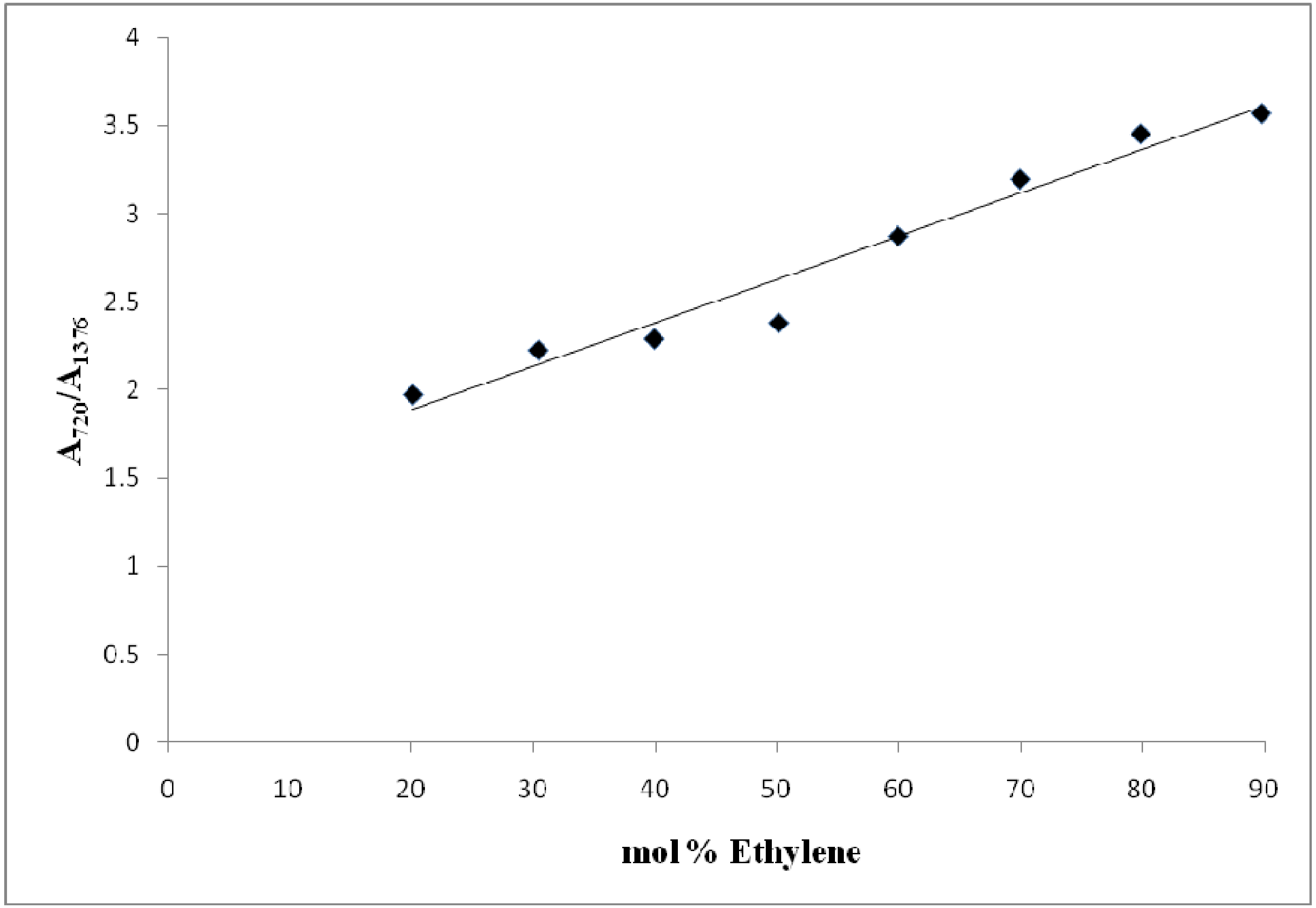


Figure 5.8: A_{720}/A_{1376} absorbance ratio versus mol % ethylene

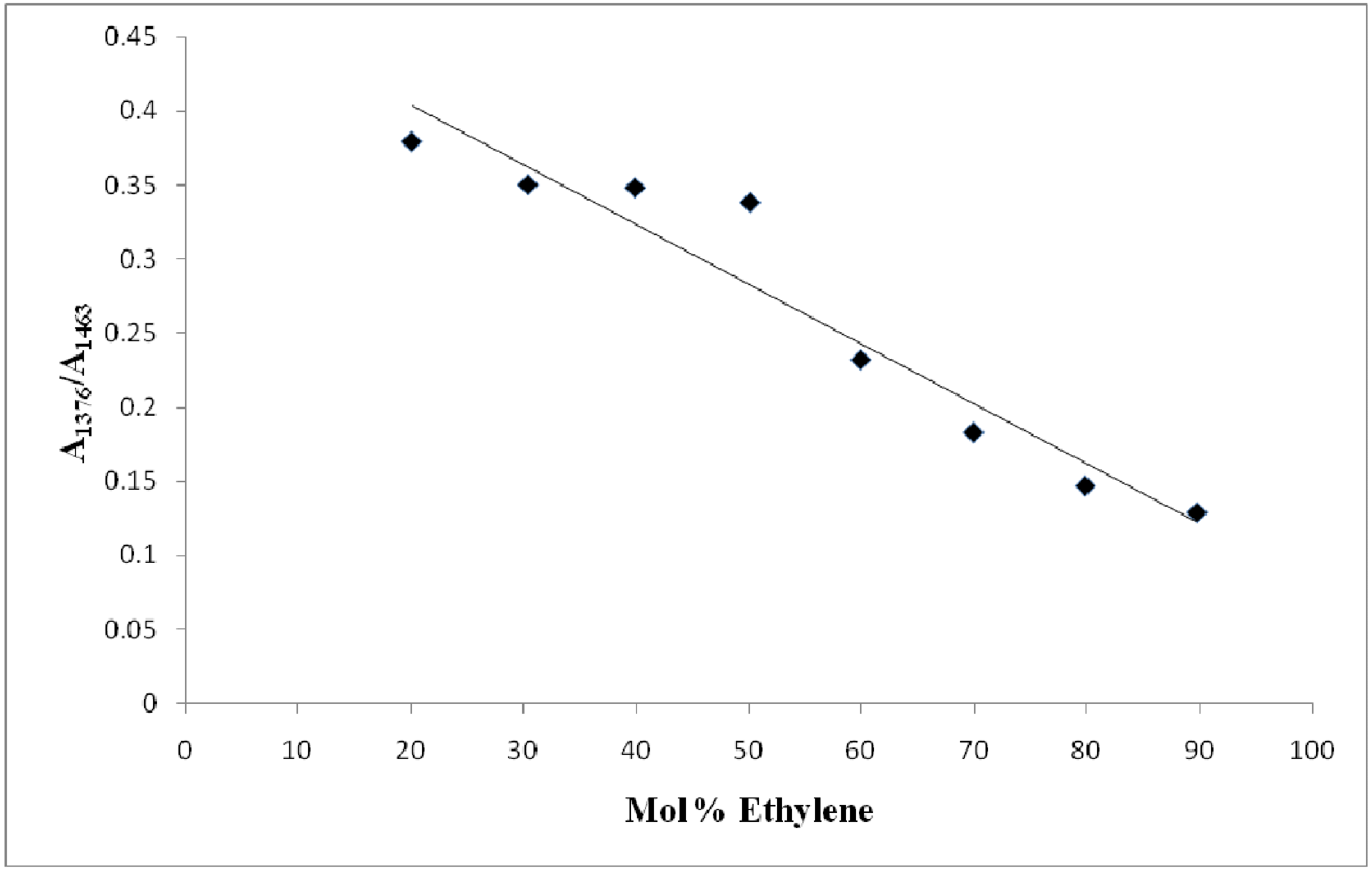


Figure 5.9: A_{1376}/A_{1463} absorbance ratio versus mol % ethylene

(b) Differential Scanning Calorimetri

Ethylene-propylene copolymer samples containing 20.1% to 89.7% ethylene were characterized using differential scanning calorimetric method. The samples were heated to 150°C at 10ºC/min and then annealed for 10 minutes before cooling back to initial temperature at the rate of 5°C/min. The samples were hold isotermally for 5 minutes at 35ºC and were then heated again to 150ºC at 10ºC/min. Table 5.6 shows the DSC analysis data for E-P copolymers prepared at constant Al/Cr ratio 30.8. The copolymers were arranged in order of decreasing ethylene content. First heating scan, cooling scan and second heating scan of E-P copolymer were shown in Figure 5.10, Figure 5.11 and Figure 5.12, respectively.

Both the melting and crystallization peaks were observed in all samples during heating and cooling scans. Copolymerization of ethylene and propylene using heterogenous catalysts normally yields block copolymers[26] with lower melting points as compared with homopolymers. The melting temperature of polyethylene prepared by the same $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ catalyst in this study is 133°C while all the E-P samples show lower melting peaks than that of polyethylene. The heating curves for E-P samples in higher propylene content consists of two or more melting peaks indicating the presence of more than one crystallites which attributable to ethylene and propylene sequence.[27] On the other hand, samples of lower mol % of propylene but rich in ethylene only show one melting peak. This indicates ethylene blocks that present in the copolymer are of almost same chain length which could crystallize at similar temperature as homopolymer.

The enthalpy of fusion of the crystallization, ΔH_c reflects the crystallinity of E-P copolymers. Decreasing enthalpy of crystallization with increasing propylene content indicates the amount of crystallinity of the monomer blocks in the samples decreases

Table 5.6: DSC analysis of ethylene-propylene copolymers prepared with different mol % monomer

% E	% P	First Heating				Cooling			Second Heating			
		Melting Temperature, T_m/ °C			ΔH/ J/g	Crystallization Temperature, T_c/ °C		- ΔH/ J/g	Melting Temperature, T_m/ °C			ΔH/ J/g
		1	2	3		1	2		1	2	3	
100.0	0.0			133	202		118	179			134	196
89.7	10.3		125	127	181		113				127	179
79.8	20.2			120	180		113				123	176
69.9	30.1			123	178		115				125	173
59.9	40.1			125	177		117	169		112	128	171
50.1	49.9		105	115	171		106	136		104	116	169
39.9	60.1	96	107	115	163		106	123	90	107	116	160
30.4	69.6			116	150		106	110		107	119	143
20.1	79.9	86	95	115	146	82	94	101	82	93	115	141

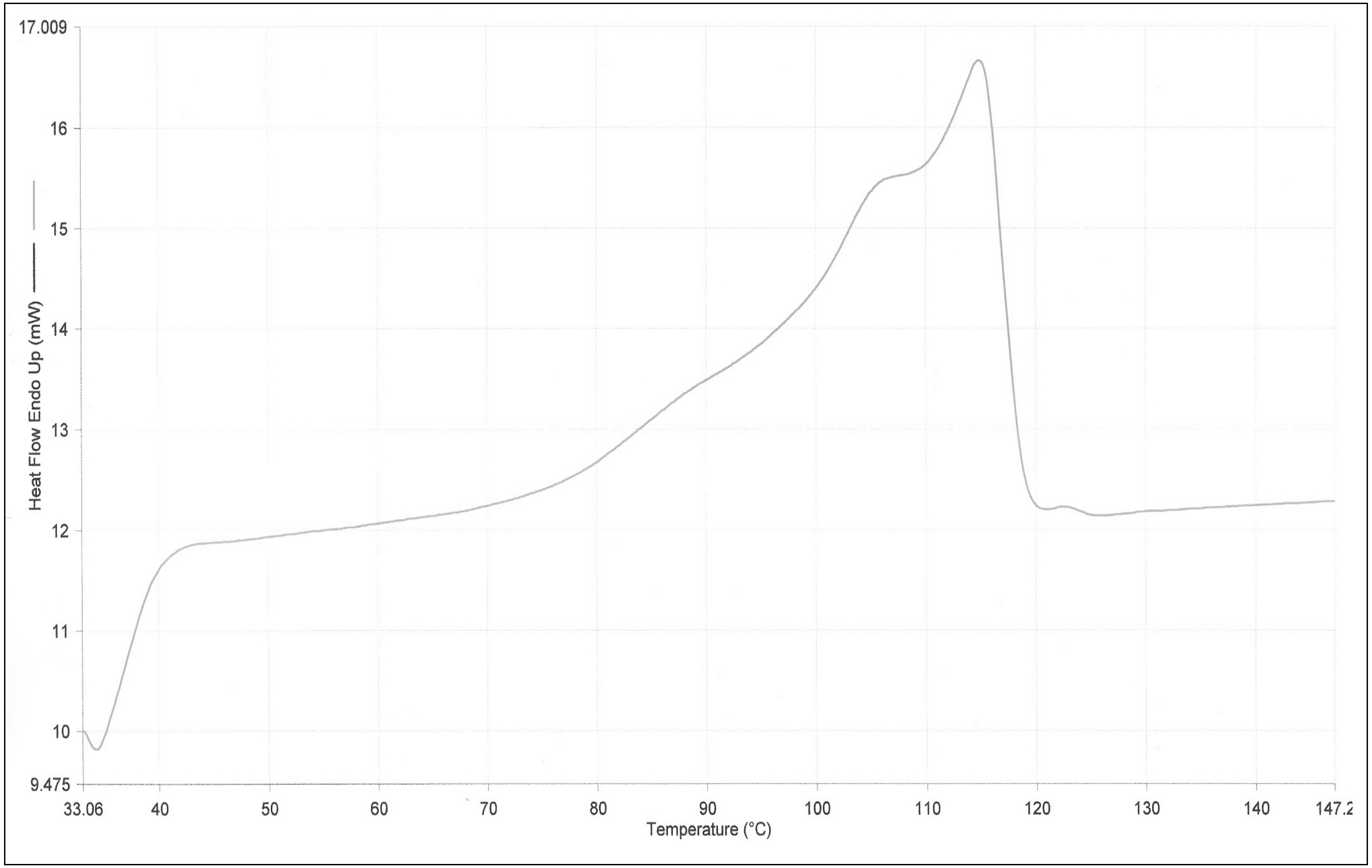


Figure 5.10: DSC first heating scan of ethylene-propylene copolymer containing 50.1% ethylene and 49.9% propylene

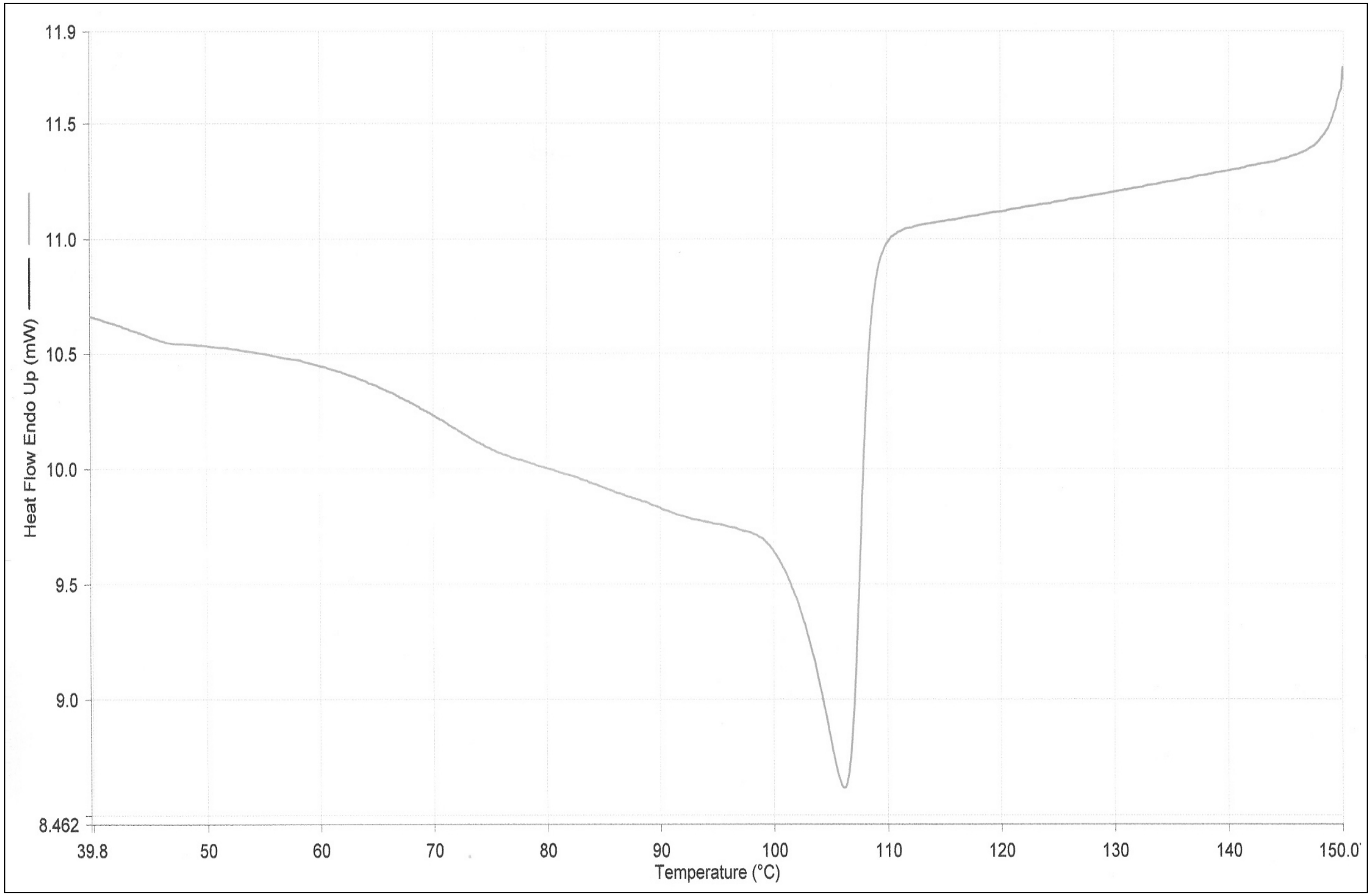


Figure 5.11: DSC cooling scan of ethylene-propylene copolymer containing 50.1% ethylene and 49.9% propylene

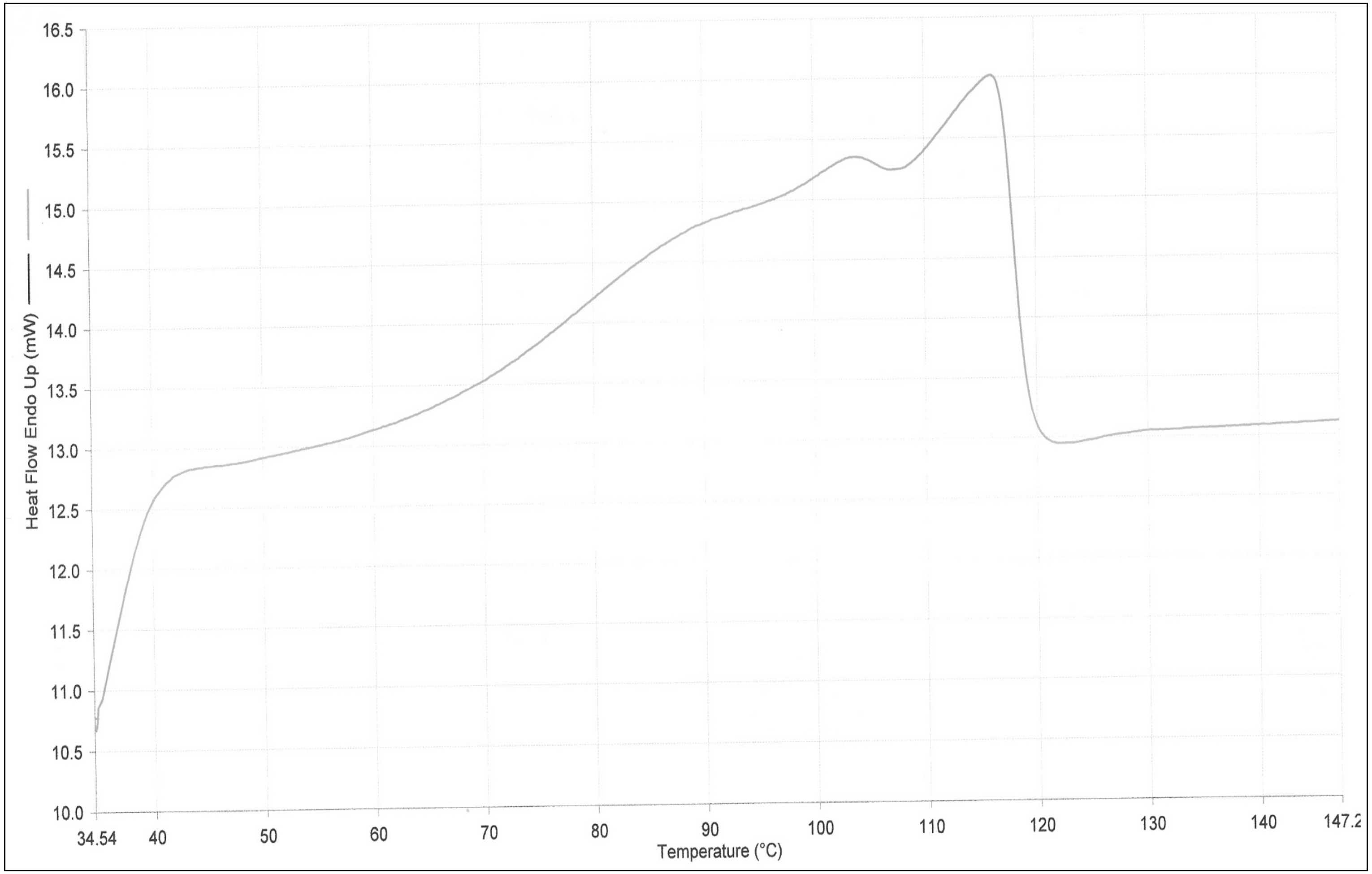


Figure 5.12: DSC second heating scan of ethylene-propylene copolymer containing 50.1% ethylene and 49.9% propylene

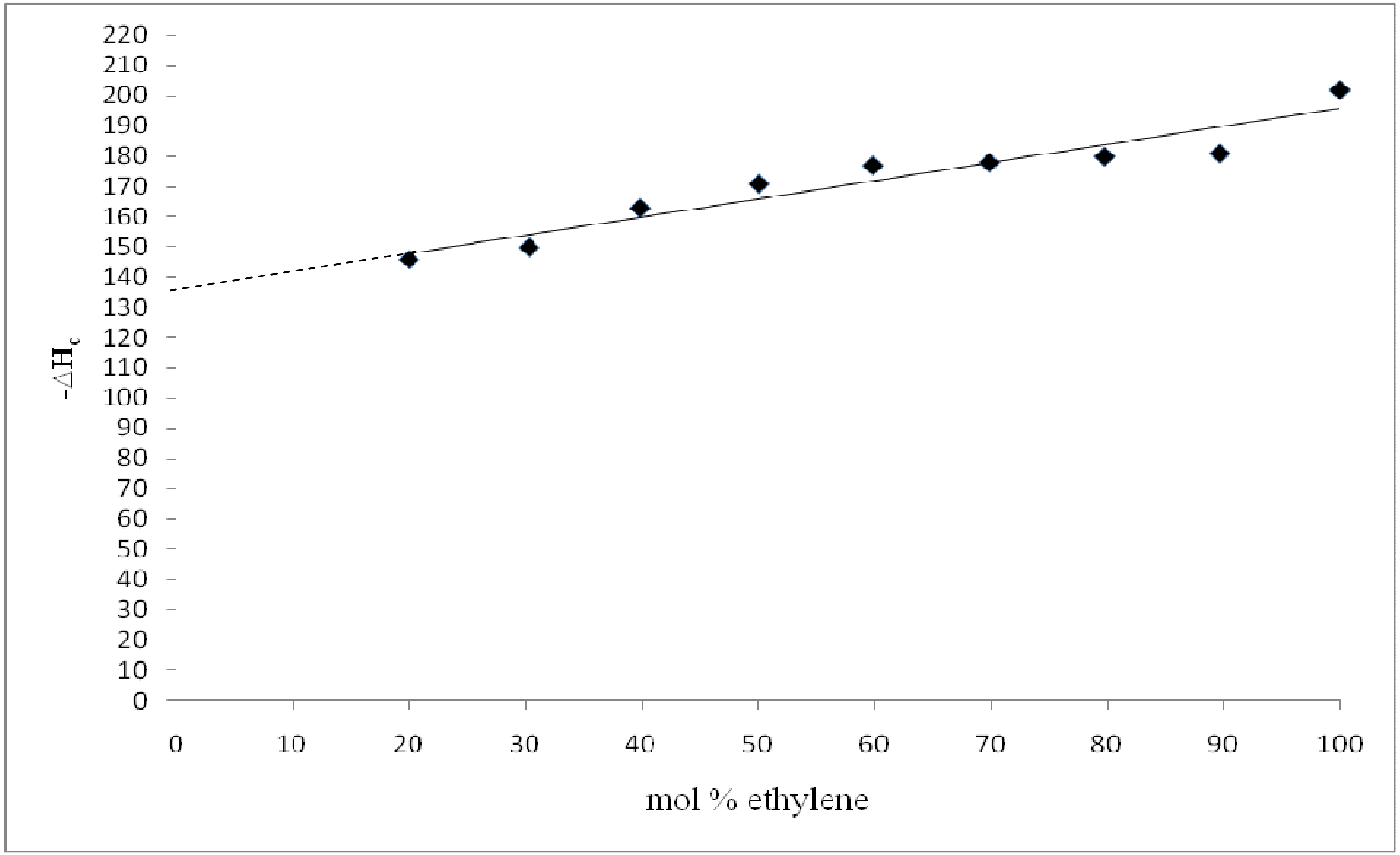


Figure 5.13: Plot of entalphy of crystallization versus mol % ethylene

thus causing the number of CH_3 groups interfering with the stereoregularity decreases.

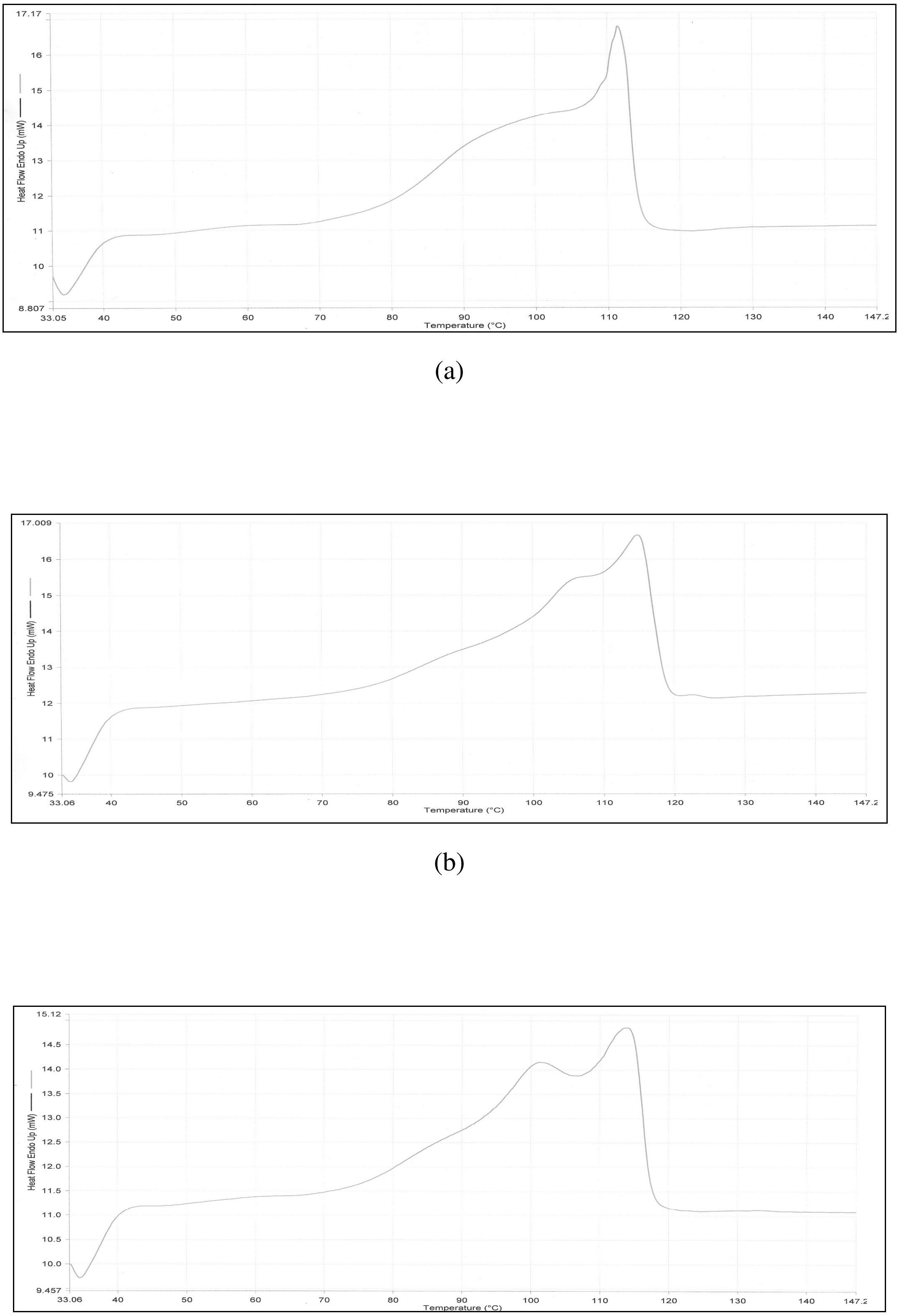
The decrease in sample crystallinity can also be explained by the difference between T_c and T_m of the polymers. For a polyethylene homopolymer prepared at Al/Cr ratio 30.8, the difference between the crystallization temperature (T_c) and the melting temperature (T_m) of a polyethylene homopolymer is 15°C. In comparison, all the ethylene-propylene copolymers at the same Al/Cr molar ratio showed a smaller difference between T_c and T_m. This is due to the fact that polyethylene sample crystallizes more readily and with greater stability than E-P copolymers.

Catalyst system in this study could not produce polypropylene homopolymer and ethylene-propylene copolymer containing 90% propylene. However, by extrapolating the value of mol % ethylene to zero as shown in Figure 5.13, entalphy of crystallization of polypropylene homopolymer can be suggested to be around 135 J/g.

Table 5.7 shows the DSC data of E-P copolymers with different aging time. Most of the samples exhibit similar melting temperature and crystallization temperature. Two melting peaks were observed in the heating curve while in the cooling scan, a sharp and well-defined crystallization peak was obtained. Influence of the catalyst-cocatalyst aging time on the DSC heating is illustrated in Figure 5.14. As the pre-reaction time of catalyst and cocatalyst increases from 30 minutes to 2 hours, the endotherm becomes broader, and also the separation between the two melting peaks becomes clearer and more intense. This observation implies that increasing aging time would increase the number of monomer block with different chain lengths that could crystallize at different temperatures.[26]

Table 5.7: DSC analysis for ethylene-propylene copolymers prepared at different aging time

Aging Time	First Heating			Cooling			Second Heating		
	Melting Temperature, T_m/ °C		ΔH/ J/g	Crystallization Temperature, T_c/ °C		- ΔH/ J/g	Melting Temperature, T_m/ °C		ΔH/ J/g
	1	2		1	2		1	2	
15	101	112	190	-	103	168	100	112	188
30	101	111	181	92	103	159	94	111	178
60	105	115	171	-	106	136	104	116	169
120	101	114	156	93	105	125	100	115	155
180	102	113	149	92	103	119	101	113	148
240	101	111	132	93	105	103	100	112	129



(a)

(b)

(c)

Figure 5.14: Comparison between DSC first heating scan of E-P copolymers prepared at different aging time: (a) 30 minutes; (b) 1 hour; (c) 2 hours

References:

1. Mirabella, F. M. J. *Polymer* 1993, **34**, 1729

2. D'Orazio, L., Mancarella, C., Martuscelli, E., Sticotti, G. and Massari, P *Polymer* 1993, **34**, 3671

3. Soga, K., Chen, S. I., Shiono, T. and Doi, Y. *Polymer*, 1985, **26**, 1888-1890

4. Gan, S. N., Chen, S. I., Ohnishi, R. and Soga, K. *Polymer*, 1987, **28**, 1391

5. Goldman, K. 'Ethylene and its Industrial Derivatives', S. A. Miller, Ed. E. Benn Publisher, London, 1969, p. 150

6. Gan, S. N., Chen, S. I., Ohnishi, R. and Soga. K. *Makromol. Chem. Rapid Commun.* 1984, **5**, 535

7. Keii, T. 'Kinetics of Ziegler-Natta Polymerization', Kodansha Ltd., Tokyo, 1972

8. Sinn, Hj., Winter, H. and von Tirpitz, W. *Makromol. Chem.* 1961, **48**, 59

9. Medalia, A. I., Orzechowski, A., Trinchera, J. A. and Morley, J. P. *J. Polymer Sci.*, 1959, **41**, 241

10. Drucker, A. and Daniel, J. H. *J. Polymer Sci.* 1959, **37**, 553

11. Bohm, L. L. *Polymer*, 1978, **19**, 553

12. Zohuri, G. H., Sadegvandi, F., Jamjah, R., Ahmadjo, S., Nekoomanesh, M. and Bigdelli, E. *J. App. Poly. Sci.* 2002, **84,** 785-790

13. Keii, T., Soga, K. and Saiki, N. *J. Polym. Sci.(C)*, 1967, **16**, 1507

14. Bohm, L. L. *Polymer*, 1978, **19**, 545

15. Schindler, A. *Polymer Letters* 1965, **3**, 793-795

16. Amberg, L. O., Robinson, A. E., *Rubber Plastics Age* 1961, **42**, 875

17. 1Eby, L. T., Fusco, J. V., *Rubber Age* 1962, **91**, 949

18. Natta, G., Crespi, G., Valvassori, A. and Sartori, G. *Rubber Chem Technol*. 1963, **36**, 1583-1668

19. Corish, P. J. and Tunnicliffe, M. E. *J. Poly. Sci: part C*, 1964, **7**, 187-202

20. Tosi, C. and Ciapelli, F. *Advanced in Polymer Science* Cantow, H. J., Ferry, J. D., Fujita, H. and Natta, G. (ed), Springer-Verlag, New York, 1972, **12**, 87-130

21. Wei, P. E., *Anal. Chem*. 1961, **33**, 215

22. Gőssl, T., *Makromol. Chem*. 1961, **42**, 1

23. Drushel, H. and Iddings, F. A. *Analy. Chem*. 1963, **35(1)**, 28-32

24. Peraldo, M. and Farina, M. *Chim. Ind. (Milan)* 1960, **42**, 1349

25. Miyazawa, T. and Ideguchi, Y. *Bull. Chem. Soc. Japan* 1964, **37**, 1065

26. Boor, J. Jr. 'Macromolecular Reviews' Peterlin, A., Goodman, M., Okamura, S. Zimm, B. H. and Mark, H. F. (ed), New York, Intersience Publication, 1967, volume 2, 115-268

27. Gan, S. N. and Burfield, D. R. *Macromolecules*, 1985, **18**, 2684-2688