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**APPENDICES**

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



**APPENDIX A**

ศูนย์วิทยทรัพยากร  
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### A.1 Area between the appropriate integration limits outlines

References Method: ASTM D5017-96

**Table A-1** Integration Limits for Ethylene copolymers\*

Copolymer	Area	Region, ppm
Ethylene-butene-1	A	41.5 to 38.5
	A'	Peak at 39.4
	B	37.8 to 36.8
	C	36.0 to 33.2
	D + E	33.2 to 25.5
	F	25.2 to 24.0
	Ethylene-hexene-1	A
B		40.5 to 39.5
C		39.5 to 37.0
D		Peak at 35.8
D + E		36.8 to 33.2
F + G		33.2 to 25.5
G		28.5 to 26.5
H		24.9 to 24.1
Ethylene-octene-1	A	41.5 to 40.5
	B	40.5 to 39.5
	C	39.5 to 37.0
	D	Peak at 35.8
	D + E	36.8 to 33.2
	F + G + H	33.2 to 25.5
	H	28.5 to 26.5
	I	25.0 to 24.0
	P	24.0 to 22.0

\*Isolated methylene carbons at 30.0 ppm.

**Table A-2** Area under peaks for each LLDPE1. C<sub>4</sub>-LLDPE

Area	Integral (1)	Integral (2)	Integral (3)	Mean	RSD,%
A	15.5365	15.5000	15.5453	15.5273	0.15
A'	0.4538	0.4579	0.4540	0.4552	0.47
B	1.4472	1.4520	1.4472	1.4488	0.19
C	31.2577	31.3717	31.3964	31.3419	0.24
D+E	713.72	713.58	713.45	713.58	0.02
F	1.3367	1.3685	1.3367	1.3473	1.37

2. C<sub>6</sub>-LLDPE

Area	Integral (1)	Integral (2)	Integral (3)	Mean	RSD,%
A	0.3041	0.3047	0.3041	0.3043	0.11
B	0.2786	0.2786	0.2786	0.2786	0.00
C	15.0238	15.0198	15.0238	15.0225	0.02
D	40.428	40.4919	40.428	40.4493	0.09
D+E	0.1935	0.1935	0.1935	0.1935	0.00
F+G	1059.84	1058.68	1059.84	1059.45	0.06
G	27.8475	27.8475	27.8475	27.8475	0.00
H	0.0999	0.0999	0.0999	0.0999	0.00

3. C<sub>8</sub>-LLDPE

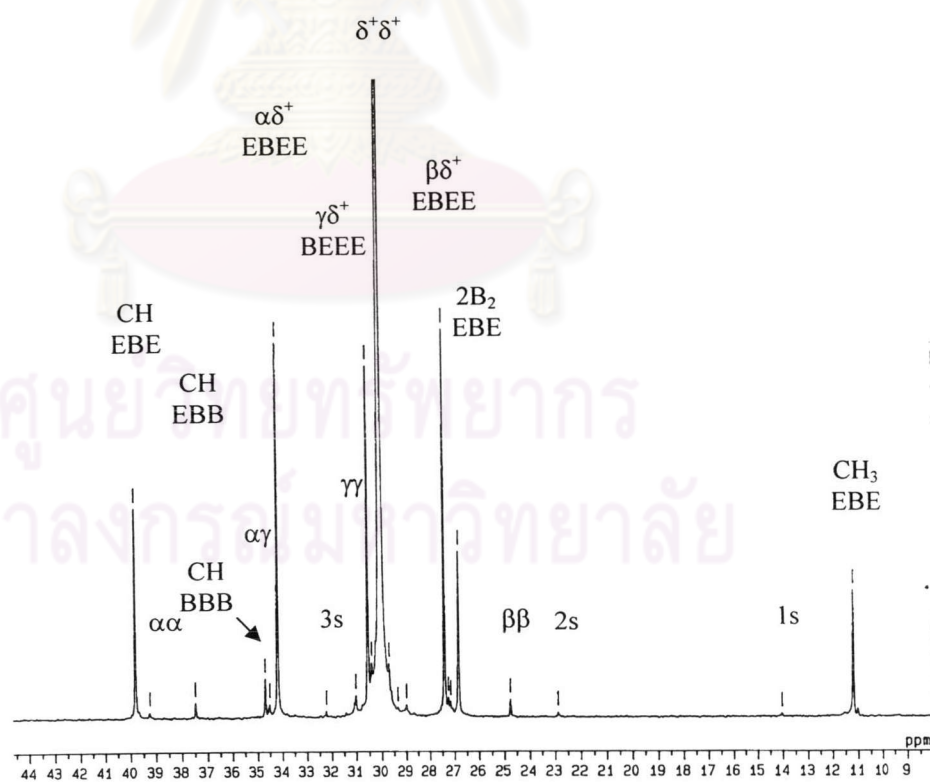
Area	Integral (1)	Integral (2)	Integral (3)	Mean	RSD, %
A	0.3781	0.3777	0.3784	0.3781	0.11
B	0.3292	0.3292	0.3292	0.3292	0.00
C	14.9900	14.9727	15.0000	14.9876	0.02
D	43.8884	43.9216	43.8884	43.8995	0.09
D+E	0.3321	0.3321	0.3321	0.3321	0.00
F+G+H	858.26	858.36	858.26	858.2933	0.06
H	39.6047	39.6480	39.5566	39.6031	0.04
I	0.4648	0.4648	0.4648	0.4648	0.00
P	12.5228	12.5228	12.5503	12.5320	0.01

**Table A-3**  $^{13}\text{C}$ -NMR chemical shifts and carbon assignments of  $\text{C}_4$ -LLDPE

Area	Chemical shift ppm	EEBEE <sup>a</sup>		EEEBEE <sup>a</sup>		EEBBEE <sup>a</sup>		EEBBBEE <sup>a</sup>	
		Type	b	Type	b	Type	b	Type	b
A	39.0-39.6	CH	1	CH	2	$\alpha\alpha$	2		1.91
A	~39.4							$\alpha\alpha\gamma$	2
B	~37.2					CH $\beta$	2	CH $\beta$	2
C	34-35	$\alpha$	2	$\alpha, \alpha\gamma$	4	$\alpha\gamma$	2	CH $\beta\beta, \alpha\gamma$	3
D	30.4	$\gamma$	2	$\gamma$	2	$\gamma$	2	$\gamma$	2
	30.0	$\delta^+, \delta^+$	3	$\delta^+, \delta^+$	3	$\delta^+, \delta^+$	3	$\delta^+, \delta^+$	3
E	27.3	$\beta$	2	$\beta$	2	$\beta$	2	$\beta$	2
	26.7	E2	1	E2	2	E2	2	E2	3
F	24.6			$\beta\beta$	1				

<sup>a</sup>Sequence units; E equals to ethene and B equals to 1-butene.

<sup>b</sup>Number of carbons.

**Figure A-1**  $^{13}\text{C}$ -NMR spectrum of whole  $\text{C}_4$ -LLDPE in *o*-dichlorobenzene at  $130^\circ\text{C}$ .

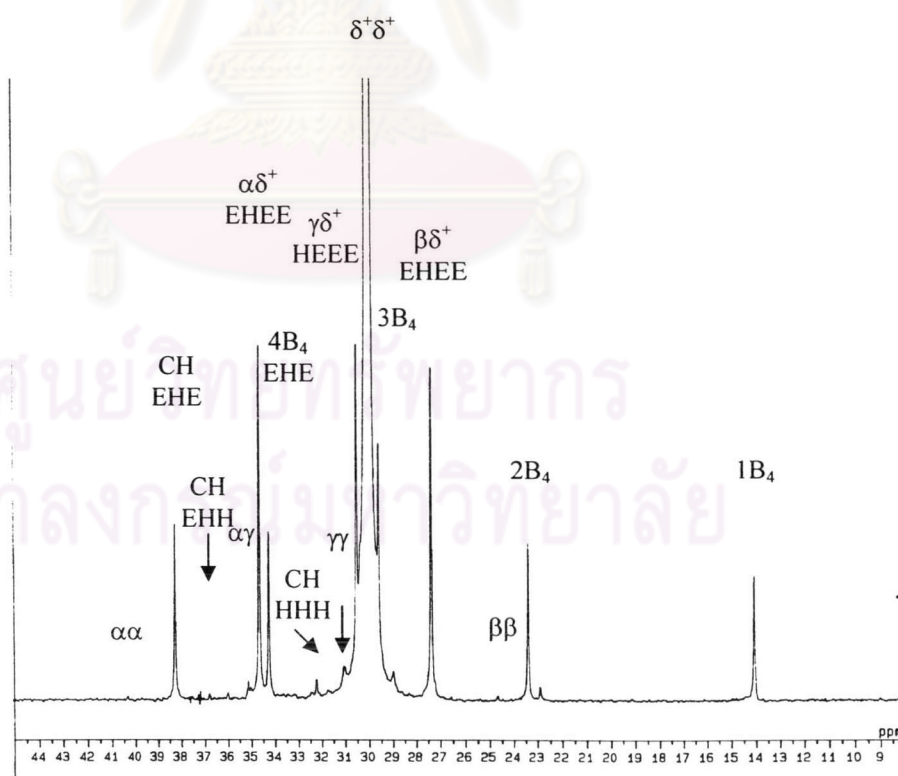


**Table A-4**  $^{13}\text{C}$ -NMR chemical shifts and carbon assignments of  $\text{C}_6$ -LLDPE

Area	Chemical shift ppm	$\text{EEHEE}^a$		$\text{EEHEHEE}^a$		$\text{EEHHHEE}^a$		$\text{EEHHHEE}^a$	
		Type	b	Type	b	Type	b	Type	b
A	~40.8							$\alpha\alpha\gamma$	2
B	~40.2					$\alpha\alpha$	1		
C	38.1	CH	1	CH	2				
D	~35.8					CH $\beta$	2		
E	34.5-35.0	$\alpha$	2	$\alpha, \alpha\gamma$	4	B4, $\alpha\gamma$	4	B4, $\alpha\gamma$	5
	34.1	B4	1	B4	2				
	33.5							CH $\beta\beta$	1
F	30.4	$\gamma$	2	$\gamma$	2	$\gamma$	2	$\gamma$	2
	30.0	$\delta, \delta$	3	$\delta, \delta$	3	$\delta, \delta$	3	$\delta, \delta$	3
	29.5	B3	1	B3	2	B3	2	B3	3
G	27.3	$\beta$	2	$\beta$	2	$\beta$	2	$\beta$	2
H	24.5			$\beta\beta$	1				

<sup>a</sup> Sequence units; E equals to ethene and H equals to 1-hexene.

<sup>b</sup> Number of carbons.

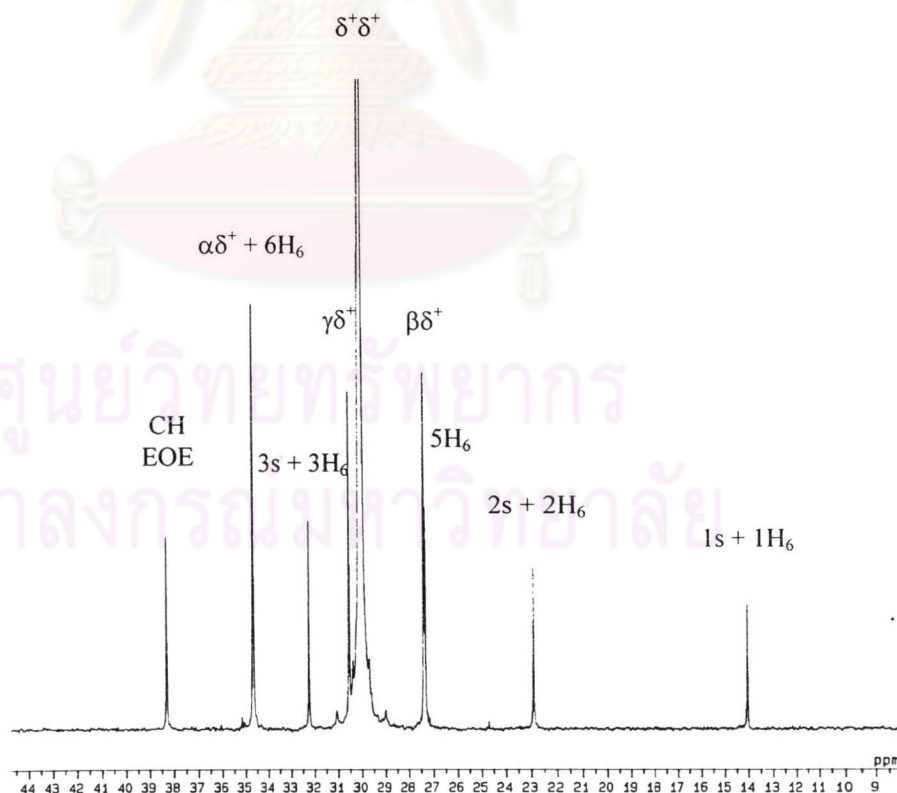
**Figure A-2**  $^{13}\text{C}$ -NMR spectrum of whole  $\text{C}_6$ -LLDPE in *o*-dichlorobenzene at  $130^\circ\text{C}$ .

**Table A-5**  $^{13}\text{C}$ -NMR chemical shifts and carbon assignments of  $\text{C}_8$ -LLDPE

Area	Chemical shift ppm	EEOEE <sup>a</sup>		EEOEOEE <sup>a</sup>		EEOOEE <sup>a</sup>		EEOOOEE <sup>a</sup>	
		Type	b	Type	b	Type	b	Type	b
A	~40.8							$\alpha\alpha\gamma$	2
B	~40.1					$\alpha\alpha$	1		
C	38.1	CH	1	CH	2				
D	35.8					$\text{CH}\beta$	2	$\text{CH}\beta$	2
E	34.5-35.2	$\text{H6}, \alpha$	3	$\text{H6}, \alpha, \alpha\gamma$	6	$\text{H6}, \alpha\delta$	4	$\text{H6}, \alpha\gamma$	5
	33.9							$\text{CH}\beta\beta$	1
F	32.2	H3	1	H3	2	H3	2	H3	3
G	30.4	$\gamma$	2	$\gamma$	2	$\gamma$	2	$\gamma$	2
	30.0	H4	1	H4	1	H4	1	H4	1
	30.0	$\delta, \delta$	3	$\delta, \delta$	3	$\delta, \delta$	3	$\delta, \delta$	3
H	27.3	$\beta$	2	$\beta$	2	$\beta$	2	$\beta$	2
	27.2	H5	1	H5	2	H5	2	H5	3
I	24.5			$\beta\beta$	1				
P	22.9	H2	1	H2	2	H2	2	H2	2

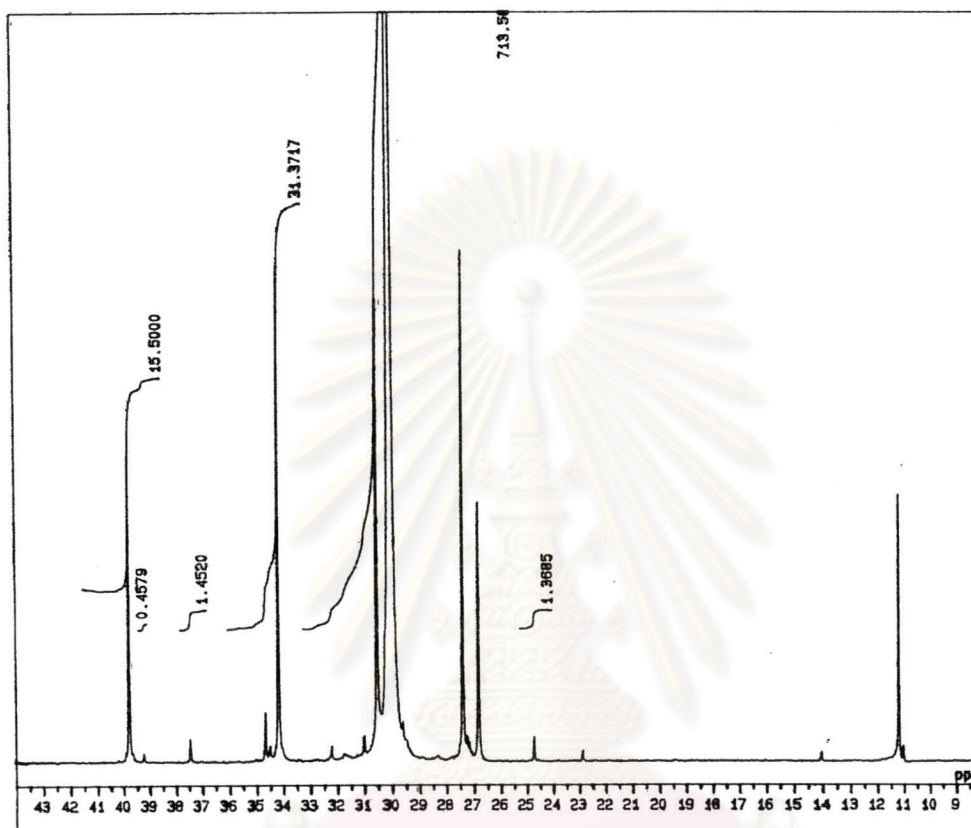
<sup>a</sup> Sequence units; E equals to ethene and O equals to 1-octene.

<sup>b</sup> Number of carbons.

**Figure A-3**  $^{13}\text{C}$ -NMR spectrum of whole  $\text{C}_8$ -LLDPE in *o*-dichlorobenzene at  $130^\circ\text{C}$ .

A2. The example calculation for branching content determination by  $^{13}\text{C}$ -NMR spectroscopy

### C<sub>4</sub>-LLDPE



From the recorded spectrum, mol% co-monomer of C<sub>4</sub>-LLDPE can be calculated by

$$\text{Mole\% butene-1} = 100\% \times B' / (B' + E')$$

When

$$B_1 = \alpha - \text{carbons: } (2A + B)/2$$

$$B_2 = \text{CH carbons: } (A' + 2B + 2C)/4$$

$$B' = \text{average moles butane-1: } (B_1 + B_2)/2$$

$$E' = \text{moles ethene: } (2D + 2E + 2F - A' - B)/4$$

Therefore, the branching content of C<sub>4</sub>-LLDPE can be calculated by



$$\text{Branching content} = \frac{1000(\text{mole\%butene-1})}{2(\text{mole\%ethene}) + 4(\text{mole\%butene-1})}$$

$$= 7.914 \text{ br/1000 Carbons}$$



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### A.3 The example of *t*-test method

**Table A-6** The branching content of fractionated C<sub>6</sub>-LLDPE different in cooling rate.

Elution temperature (°C)	Cooling rate (°C/h)		Difference (D <sub>i</sub> )
	1	2	
40	6.127	6.147	0.02
70	5.584	5.585	0.001
80	5.656	5.660	0.004
90	5.050	5.040	-0.01
100	4.641	4.641	0.0

Average            0.003  
SD                    0.0109

$$\begin{aligned}
 t_{\text{observe}} &= D/SD \times (n)^{1/2} \\
 &= (0.003/0.0109) \times (5)^{1/2} \\
 &= 0.6175
 \end{aligned}$$

There are 4 degree of freedom so the critical value of *t*/ from *t*-table is 2.78 (*p*=0.05). The observed value of *t*/ from calculation is 0.62 which is less than the critical value so the null hypothesis is accepted: the mean branching content of C<sub>6</sub>-LLDPE operated with cooling rate at 1 °C/h and 2 °C/h are not different from each other.

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**Table A-7** The *t*-distribution

Value of <i>t</i> for a confidence interval of	90%	95%	98%	99%
Critical value of <i>t</i> for <i>P</i> values of	0.1	0.05	0.02	0.01
Number of degrees of freedom				
1	6.31	12.71	31.82	63.66
2	2.92	4.3	6.96	9.92
3	2.35	3.18	4.54	5.84
4	2.13	2.78	3.75	4.6
5	2.02	2.57	3.36	4.03
6	1.94	2.45	3.14	3.71
7	1.89	2.36	3	3.5
8	1.86	2.31	2.9	3.36
9	1.83	2.26	2.82	3.25
10	1.81	2.23	2.76	3.17
12	1.78	2.18	2.68	3.05
14	1.76	2.14	2.62	2.98
16	1.75	2.12	2.58	2.92
18	1.73	2.1	2.55	2.88
20	1.72	2.09	2.53	2.85
30	1.7	2.04	2.46	2.75
50	1.68	2.01	2.4	2.68
	1.64	1.96	2.33	2.58

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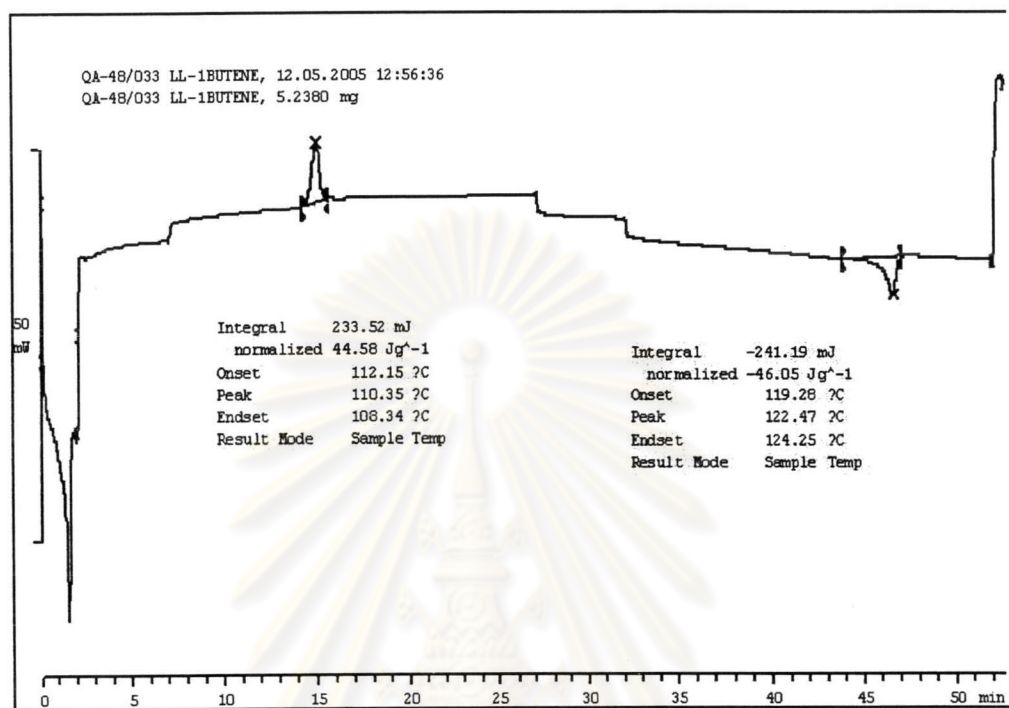
**APPENDIX B**

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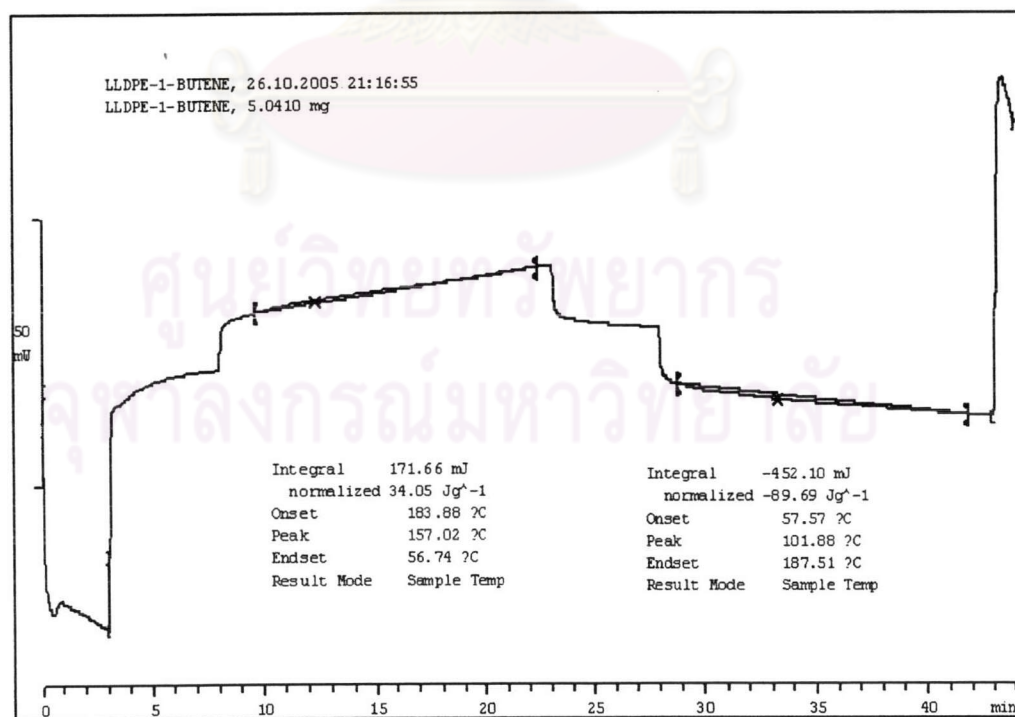


## B.1 Thermal Properties by DSC of LLDPEs

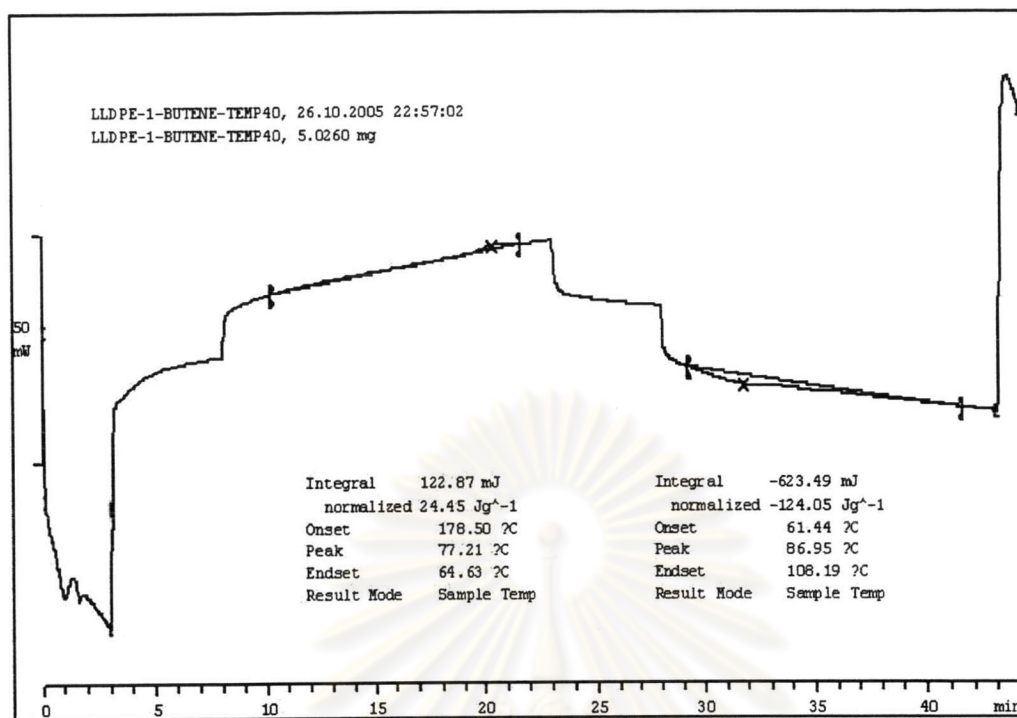
### 1. C<sub>4</sub>-LLDPE



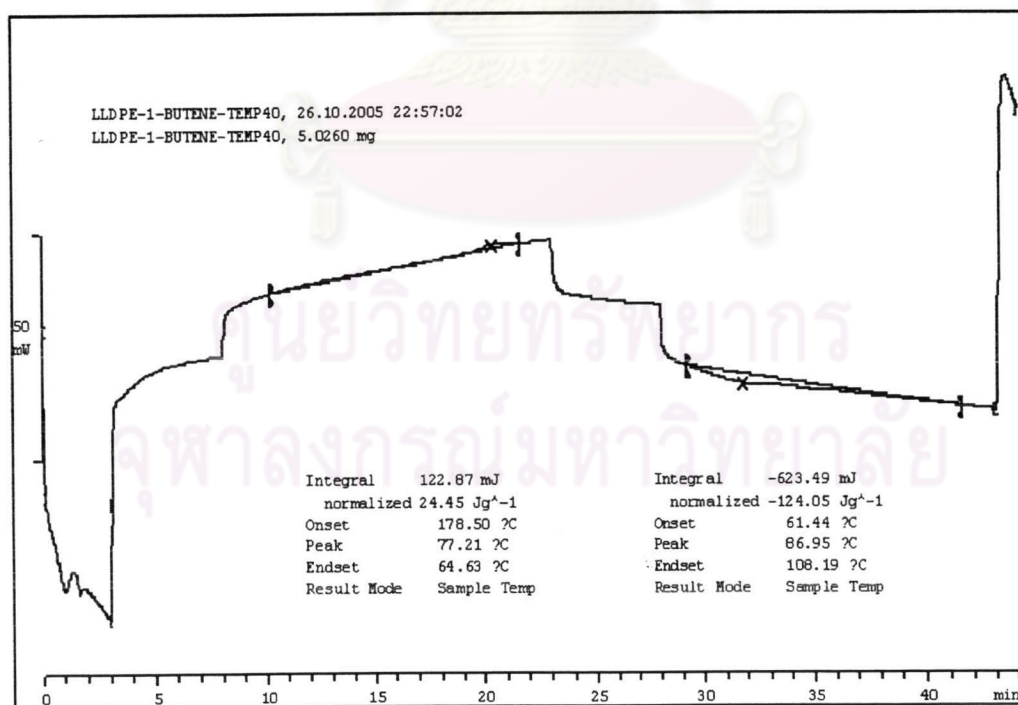
**Figure B.1** DSC thermogram on heating curve of whole C<sub>4</sub>-LLDPE.



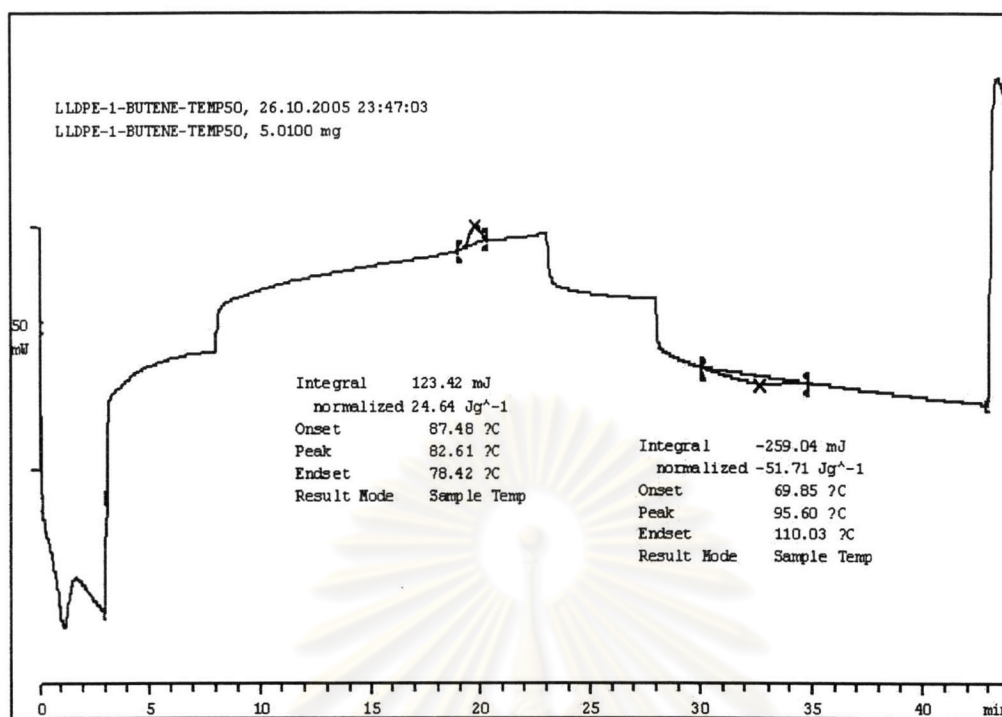
**Figure B.2** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 20°C.



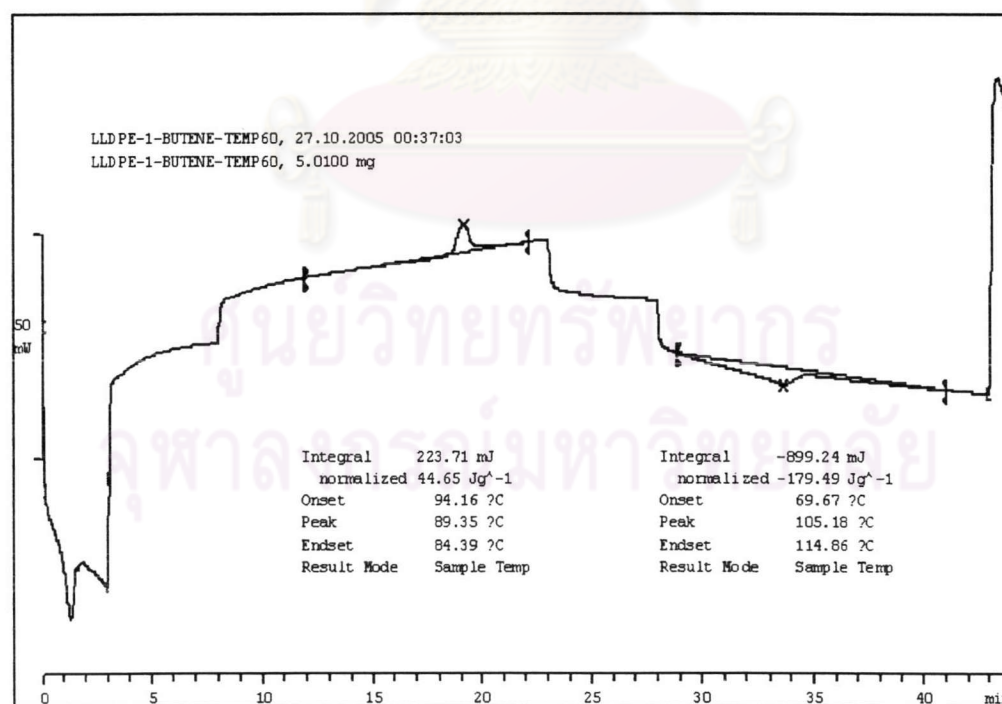
**Figure B.3** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 30°C.



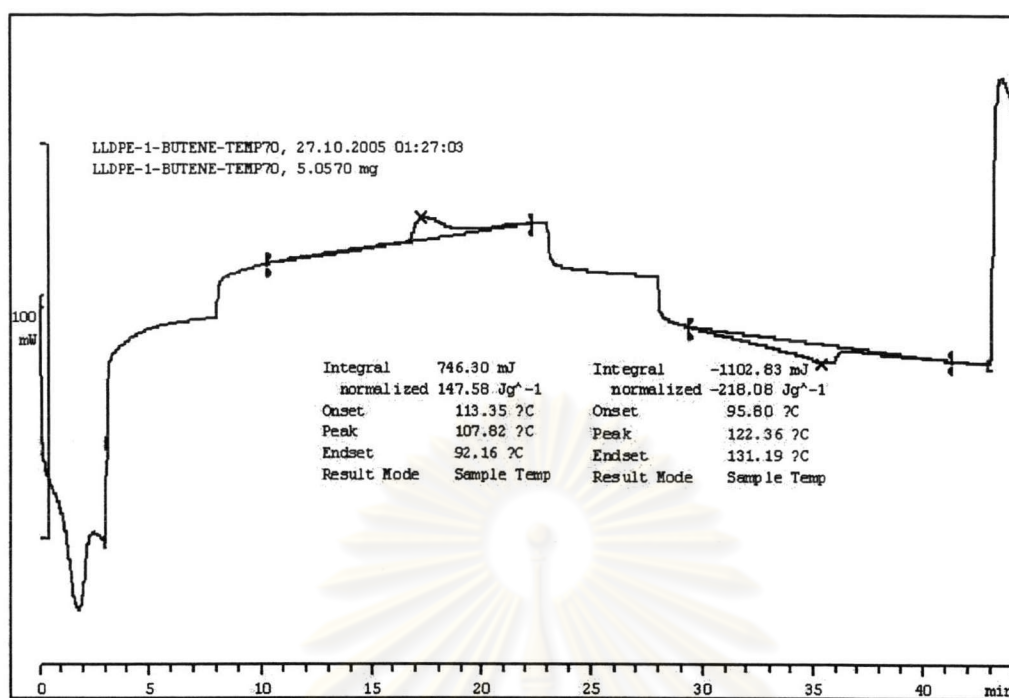
**Figure B.4** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 40°C.



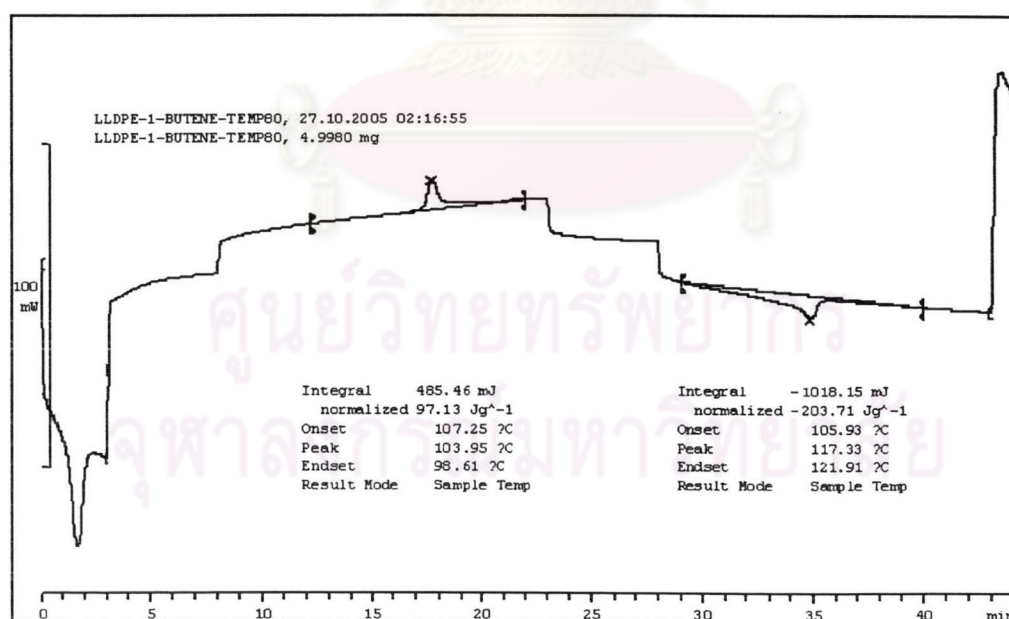
**Figure B.5** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 50°C.



**Figure B.6** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 60°C.

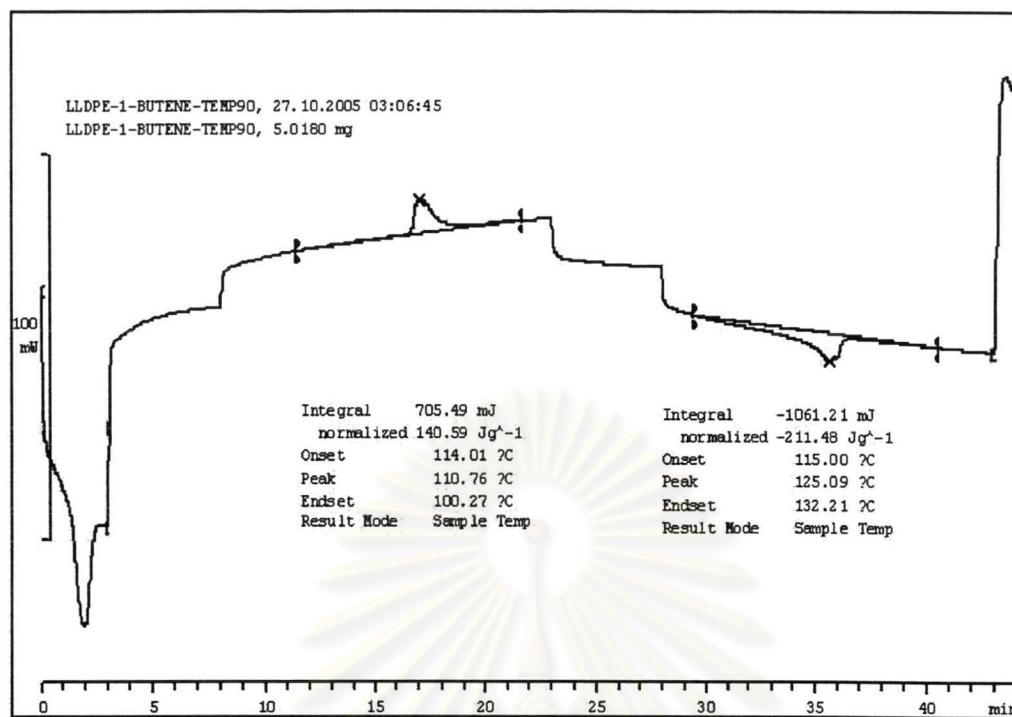


**Figure B.7** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 70°C.

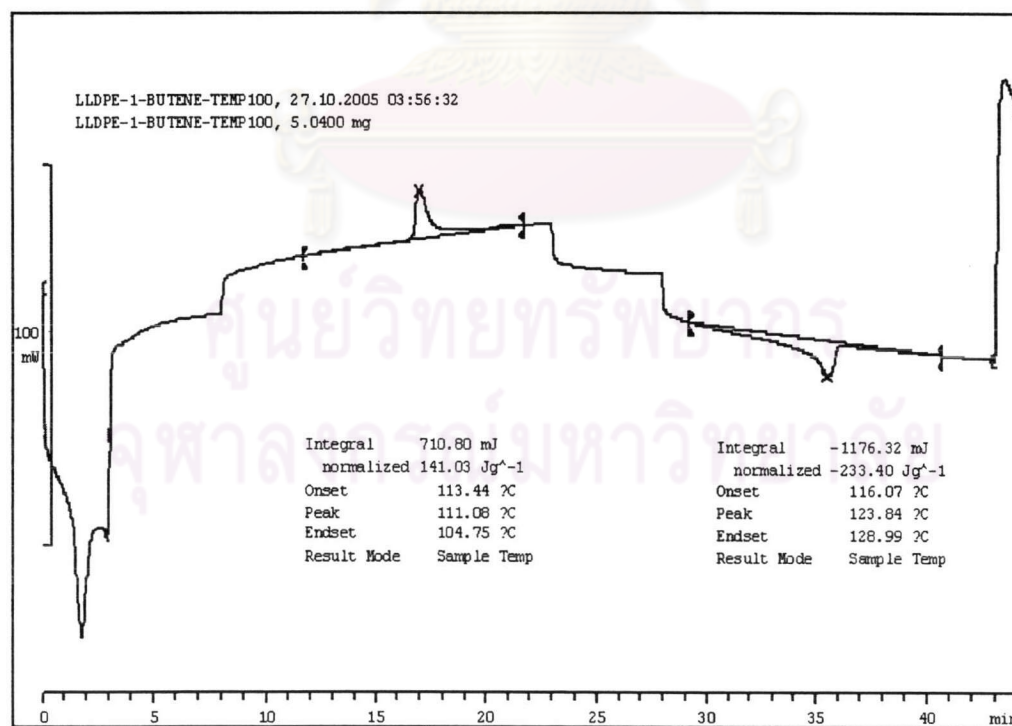


**Figure B.8** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 80°C.

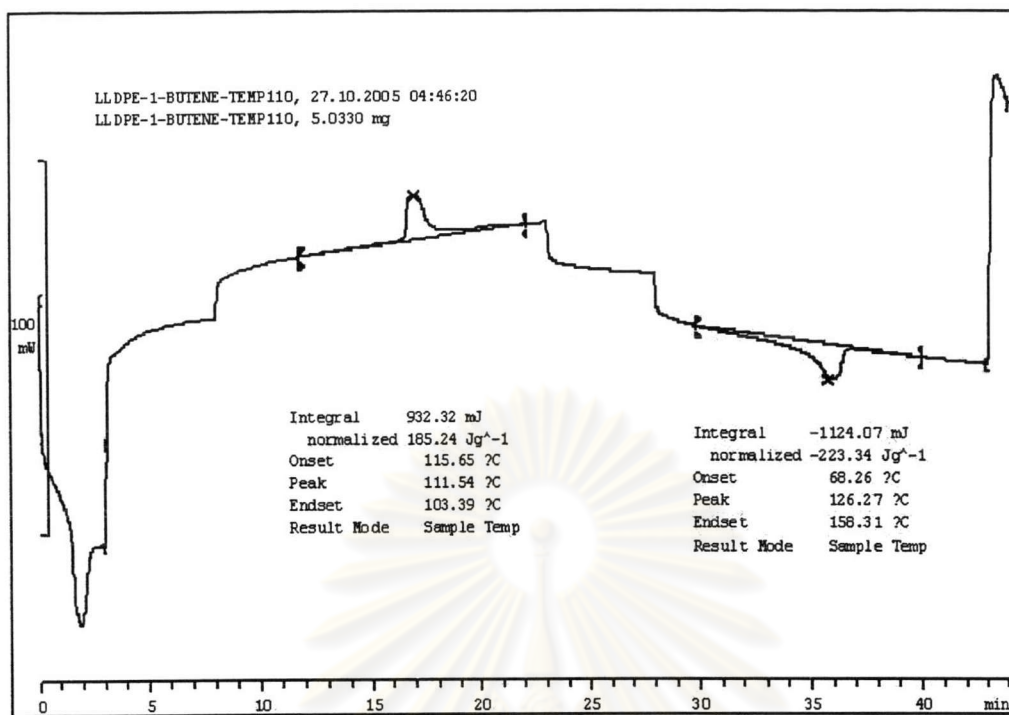




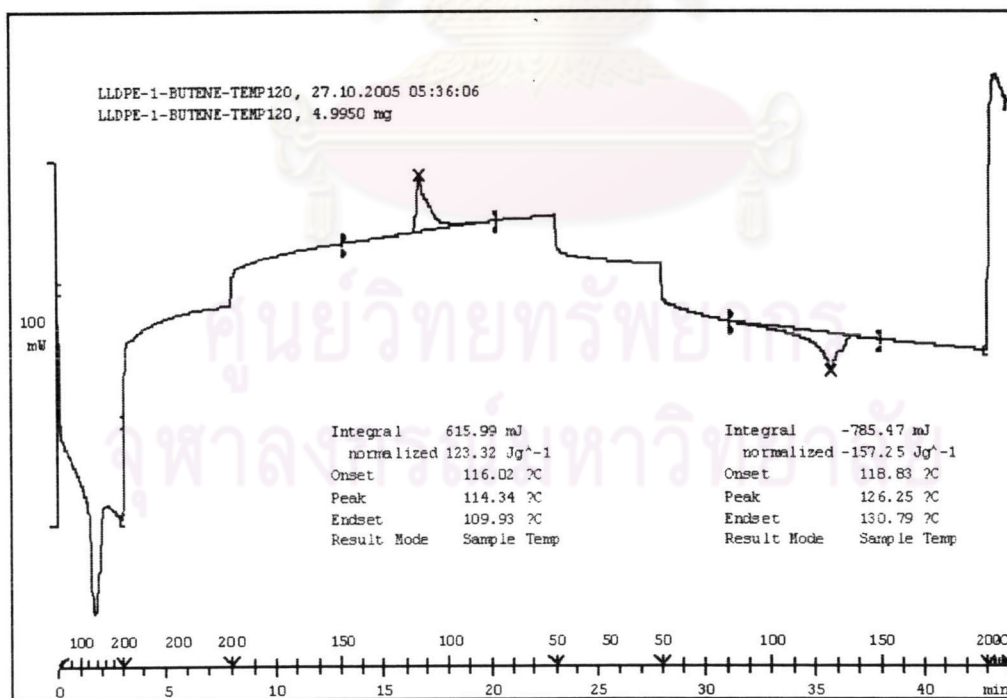
**Figure B.9** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 90°C.



**Figure B.10** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 100°C.



**Figure B.11** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 110°C.



**Figure B.12** DSC thermogram on heating curve of fractionated C<sub>4</sub>-LLDPE at elution temperature 120°C.

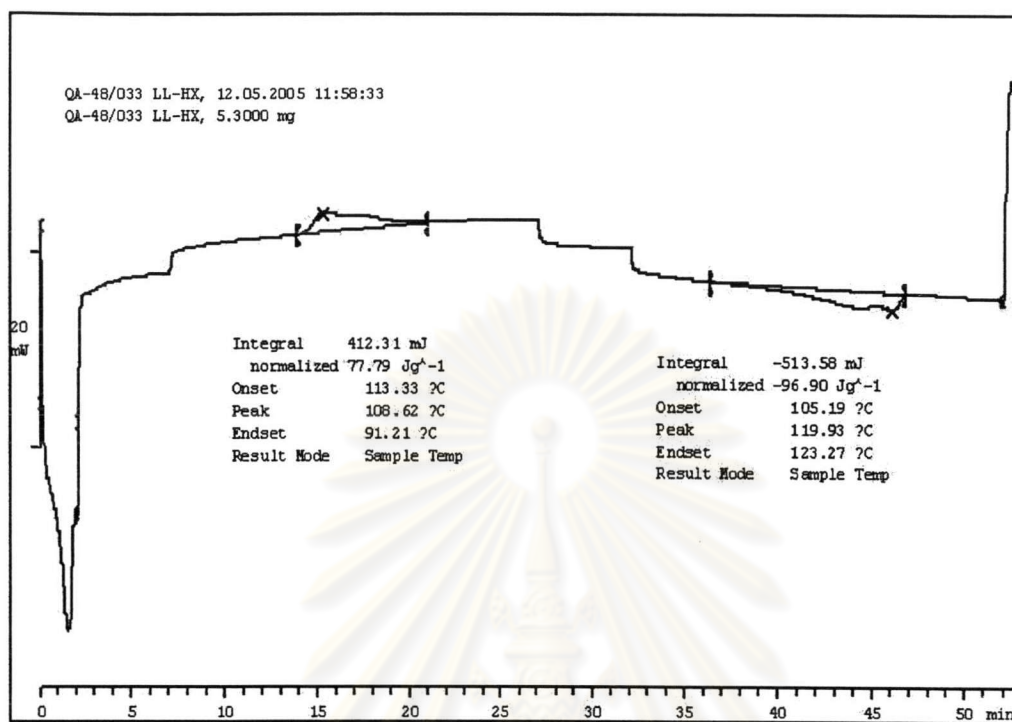
2. C<sub>6</sub>-LLDPE

Figure B.13 DSC thermogram on heating curve of whole C<sub>6</sub>-LLDPE.

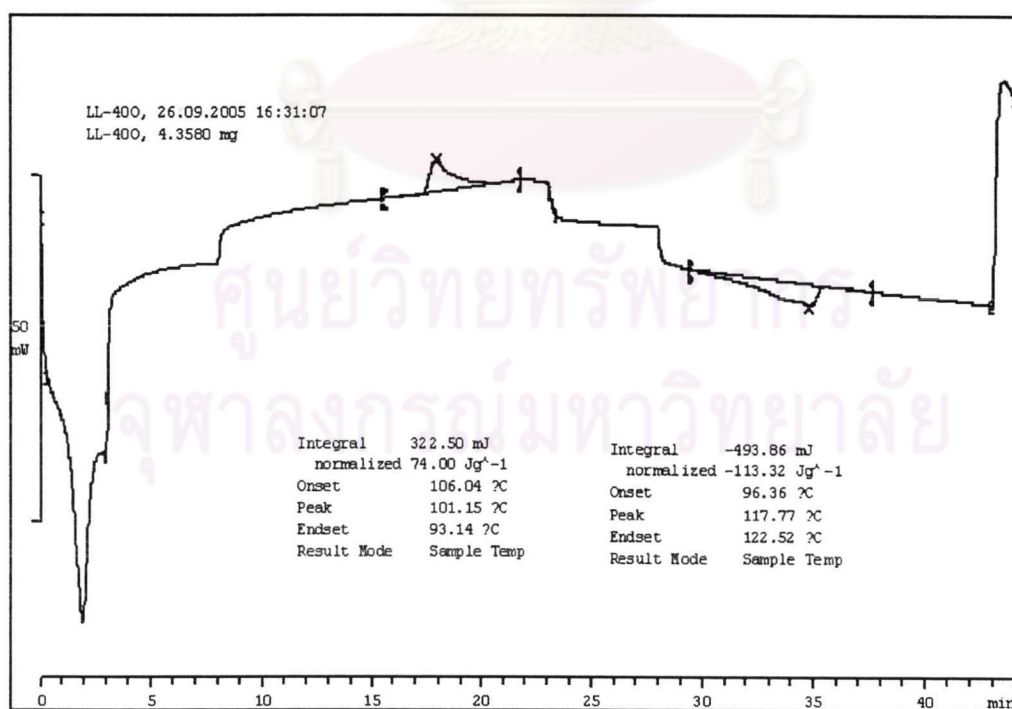
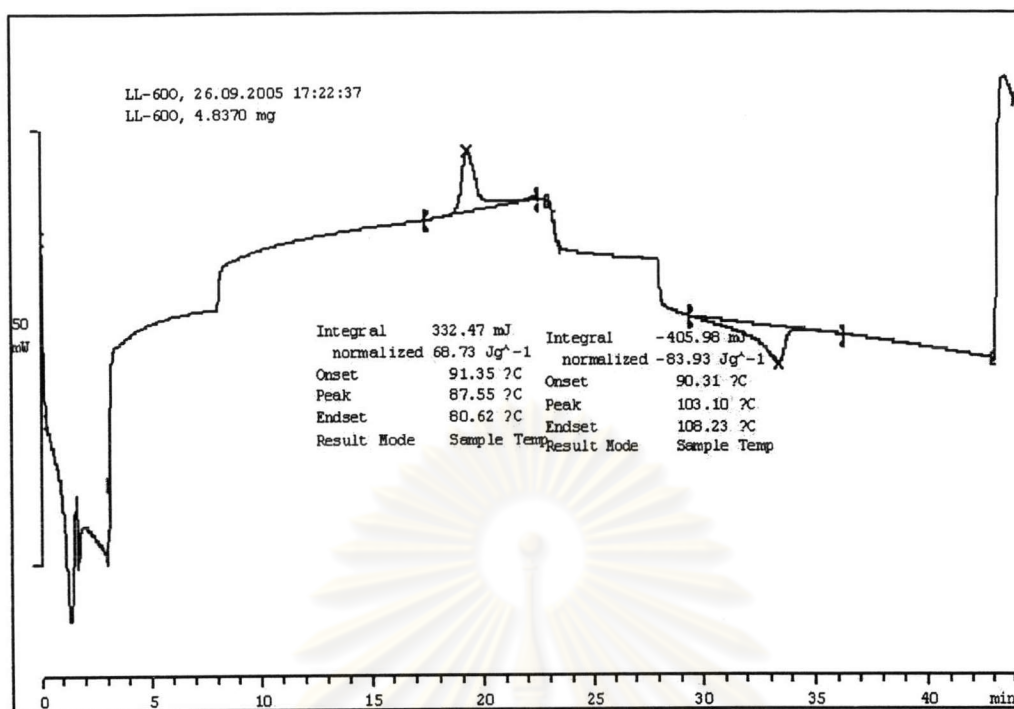
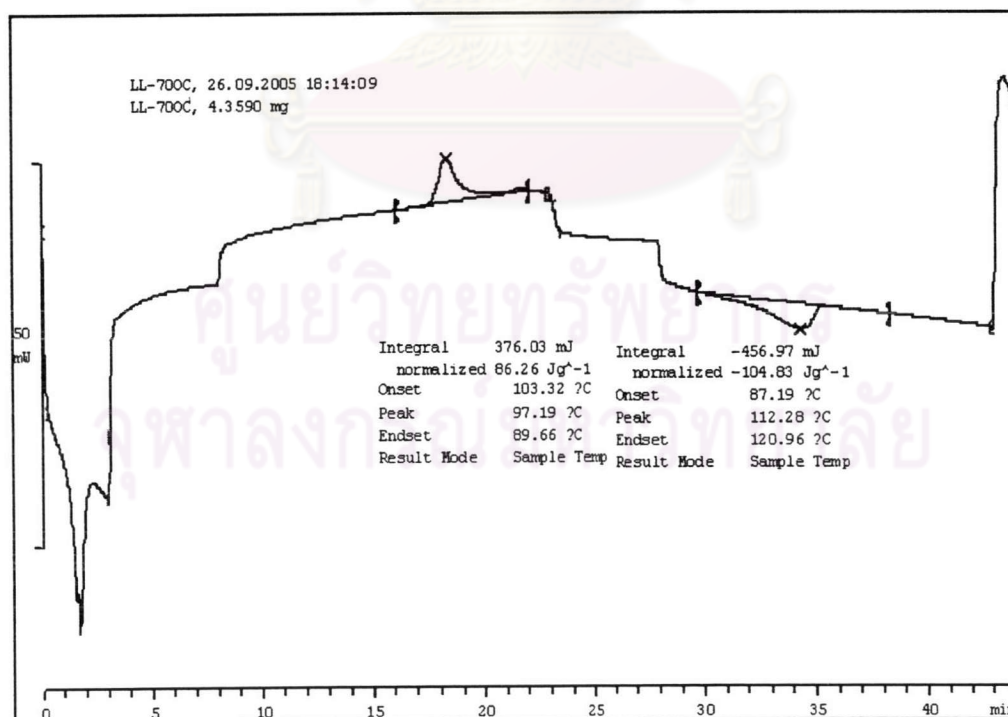


Figure B.14 DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 40°C.

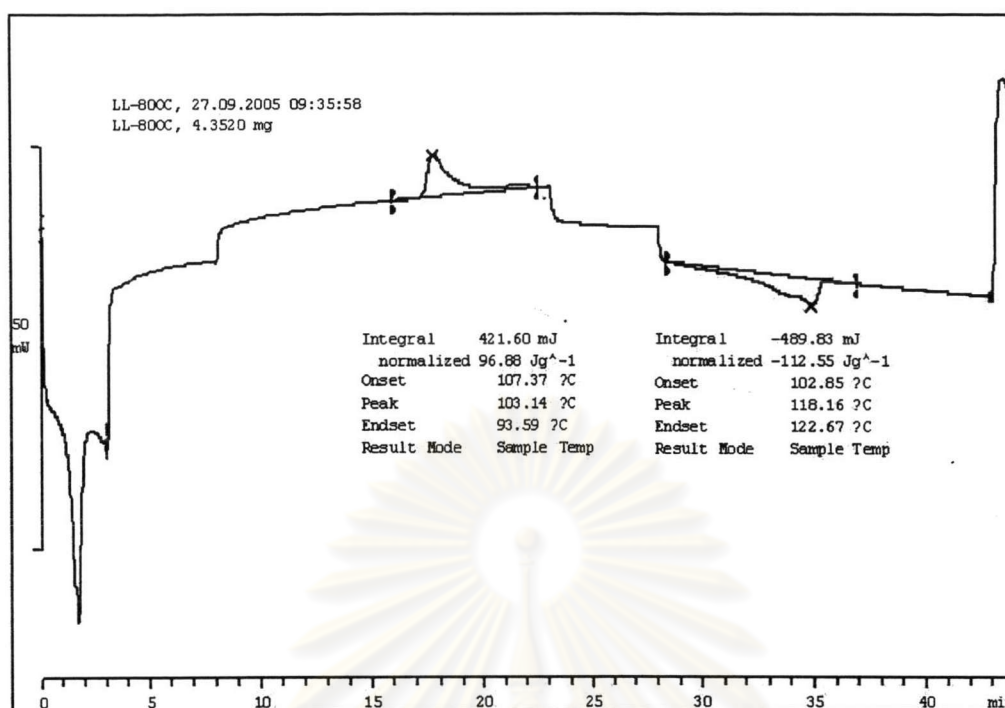


**Figure B.15** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 60°C.

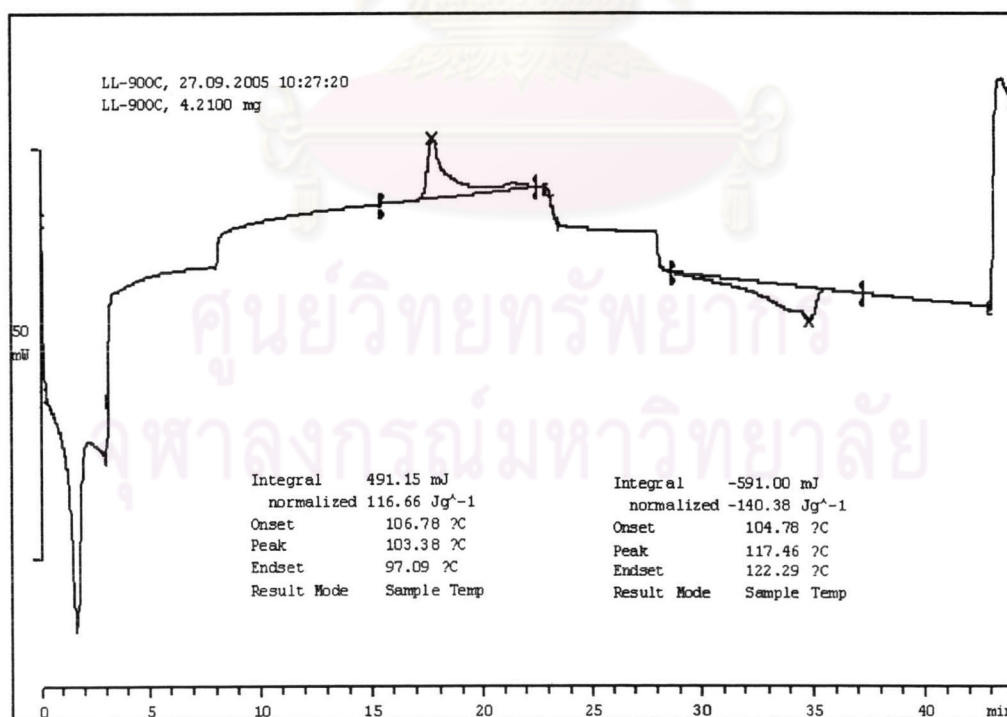


**Figure B.16** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 70°C.

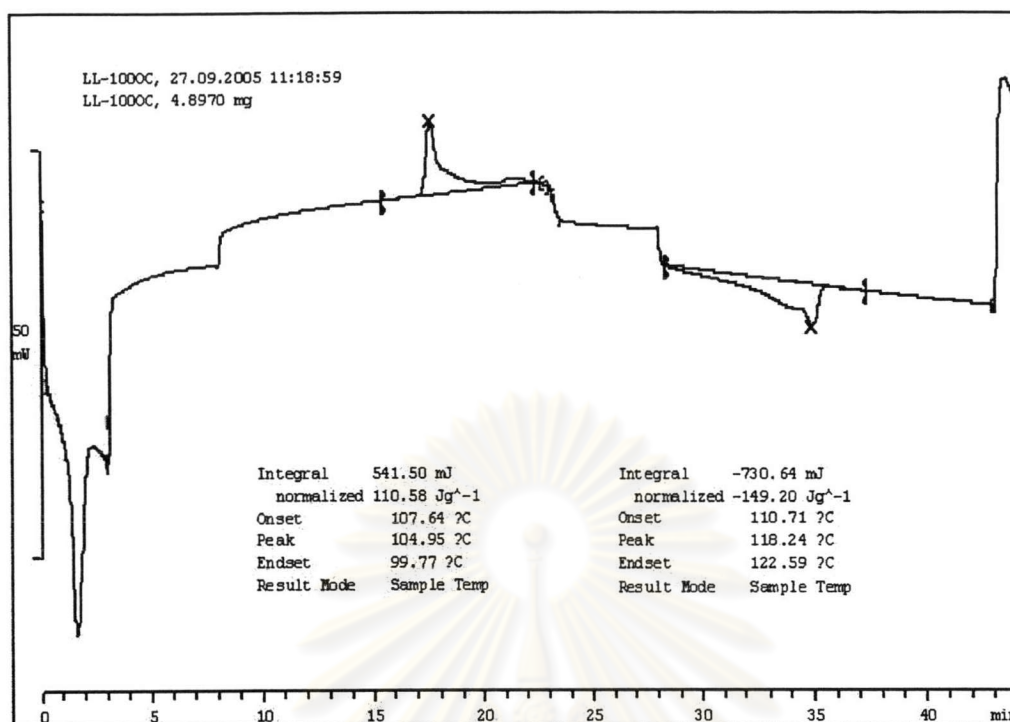




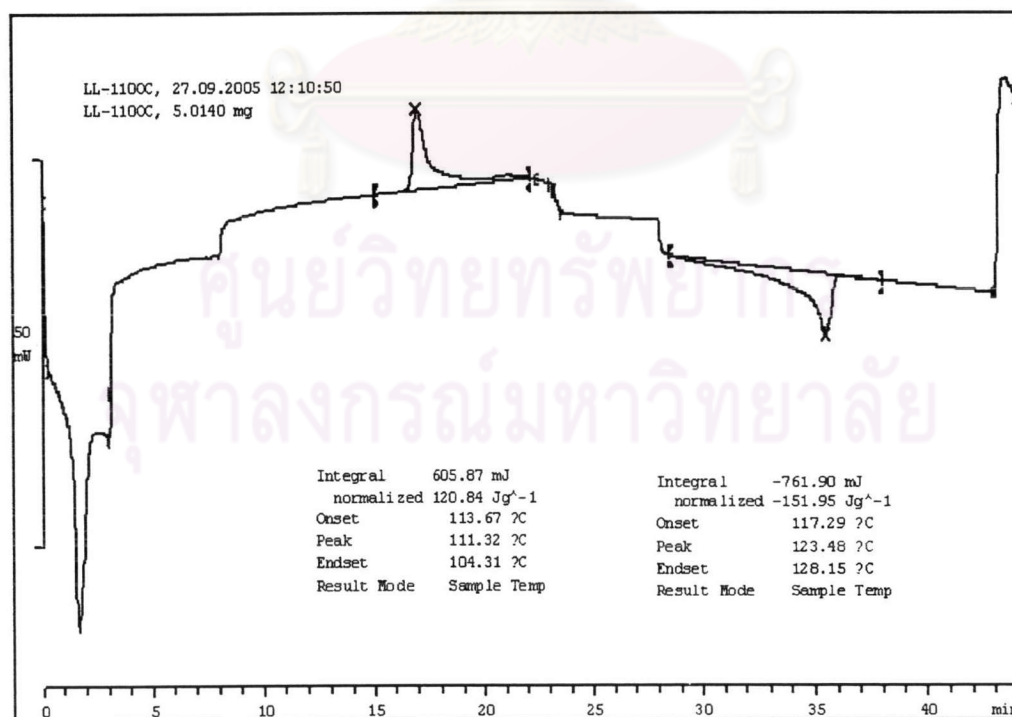
**Figure B.17** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 80°C.



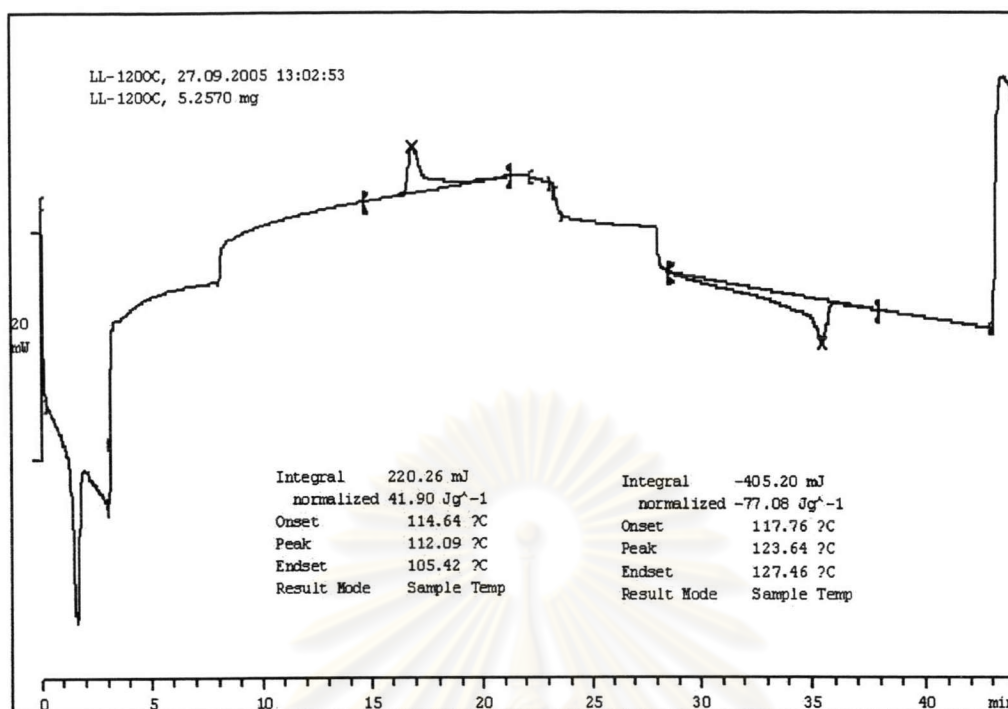
**Figure B.18** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 90°C.



**Figure B.19** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 100°C.

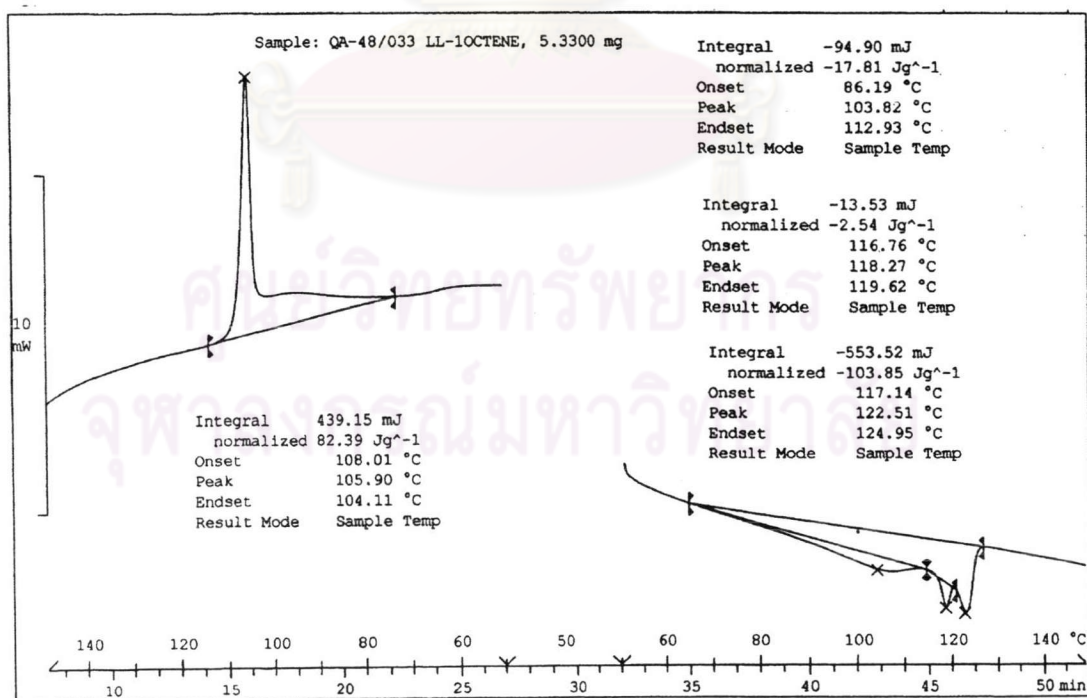


**Figure B.20** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 110°C.

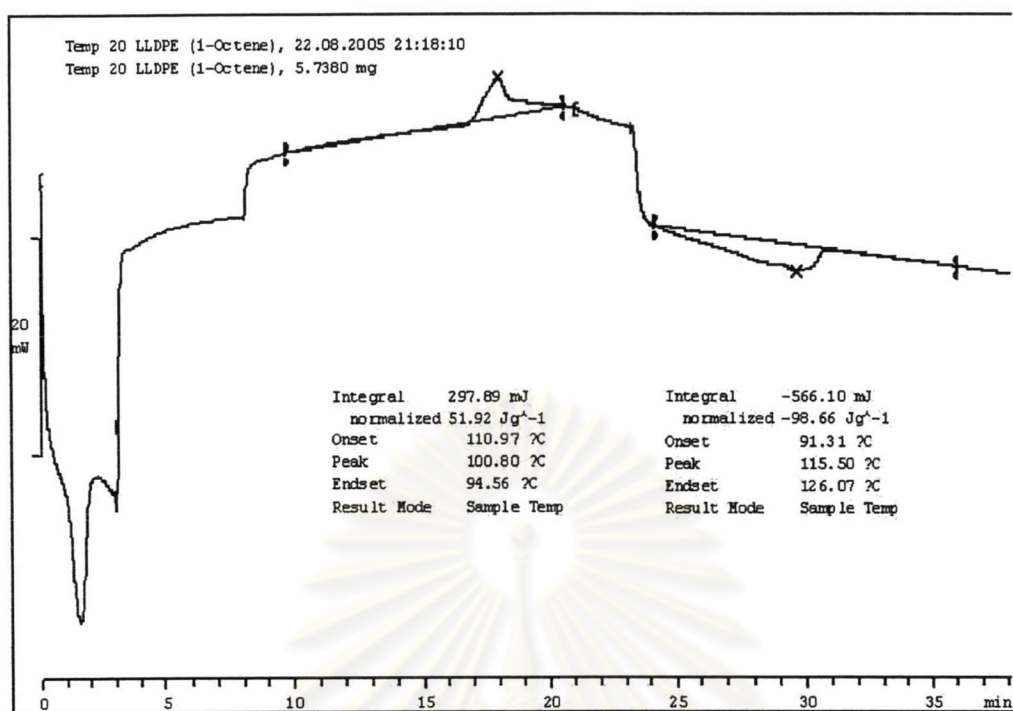


**Figure B.21** DSC thermogram on heating curve of fractionated C<sub>6</sub>-LLDPE at elution temperature 120°C.

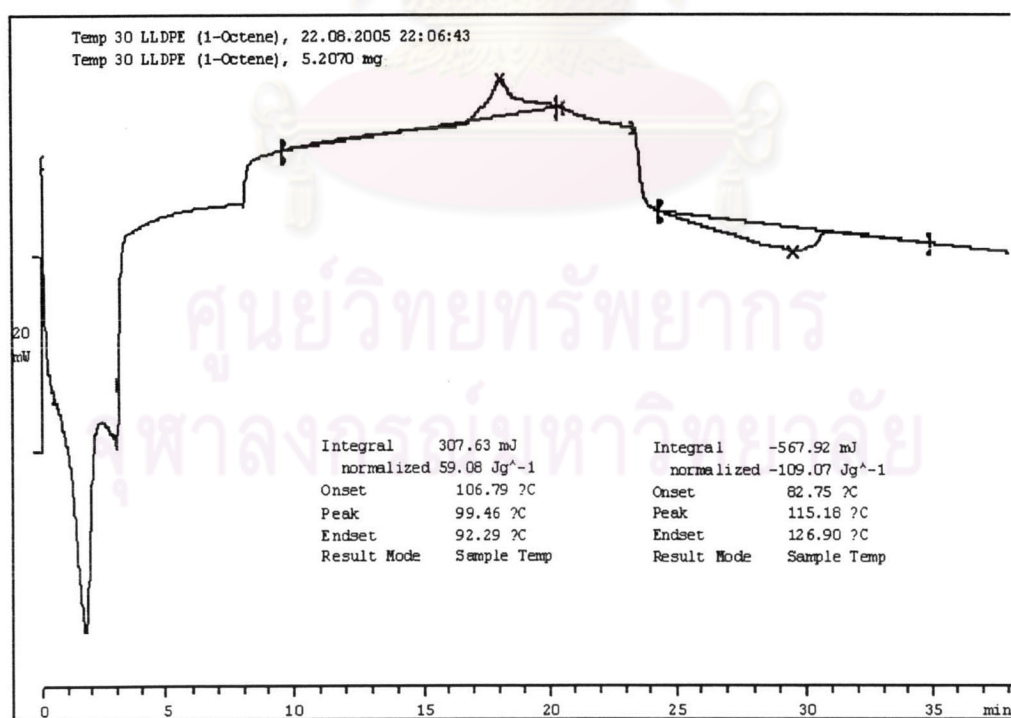
### 3. C<sub>8</sub>-LLDPE



**Figure B.22** DSC thermogram on heating curve of whole C<sub>8</sub>-LLDPE.

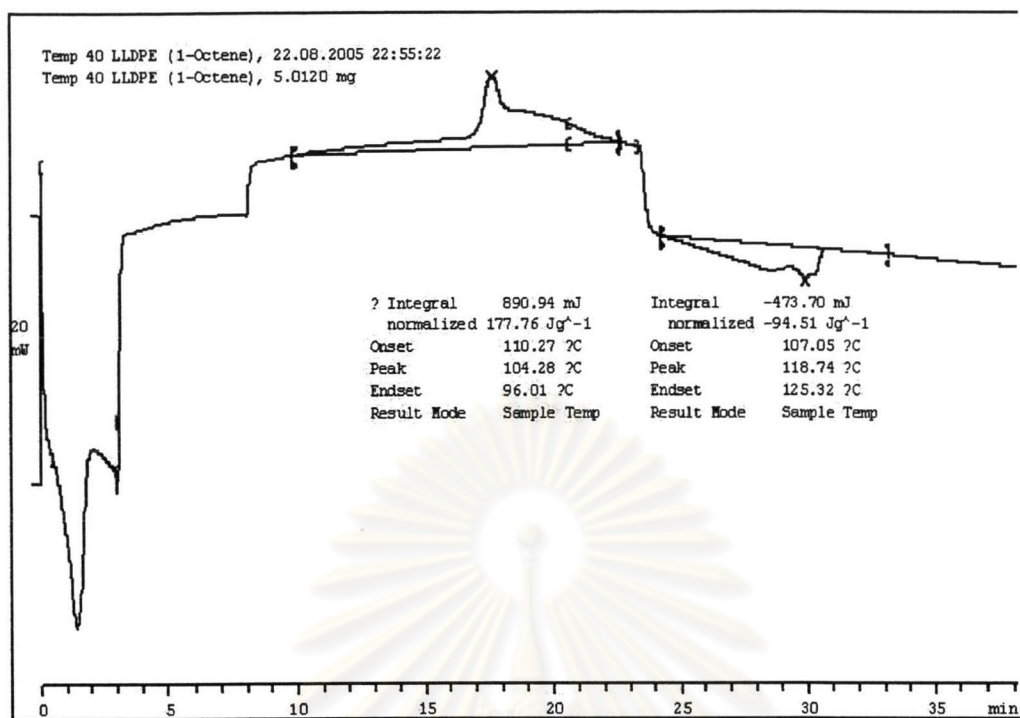


**Figure B.23** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 20°C.

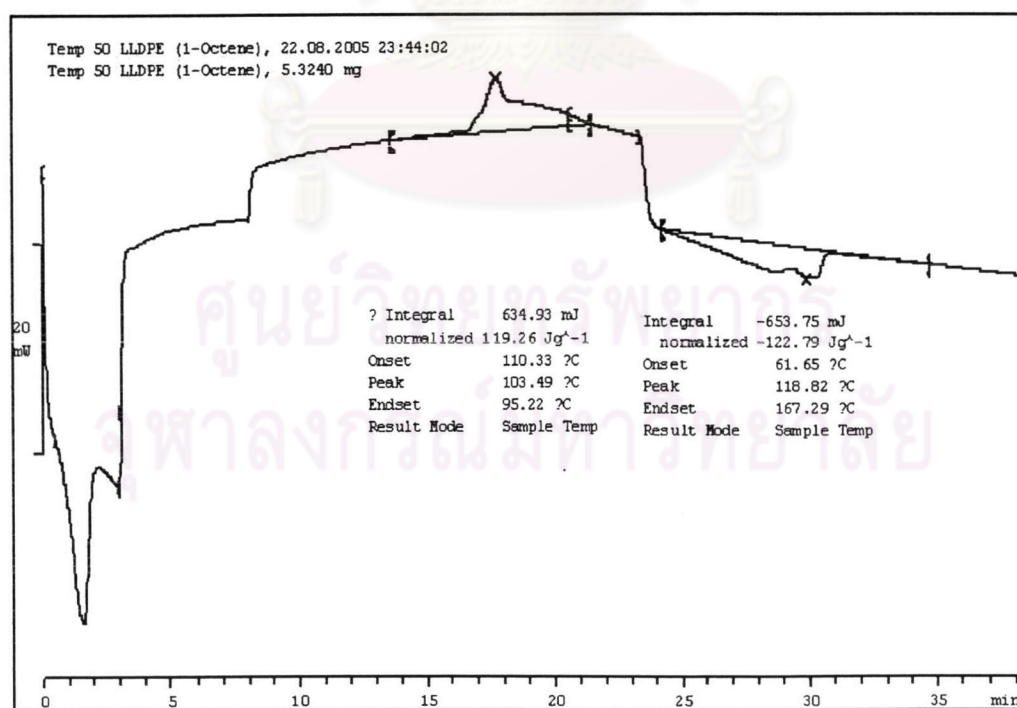


**Figure B.24** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 30°C.

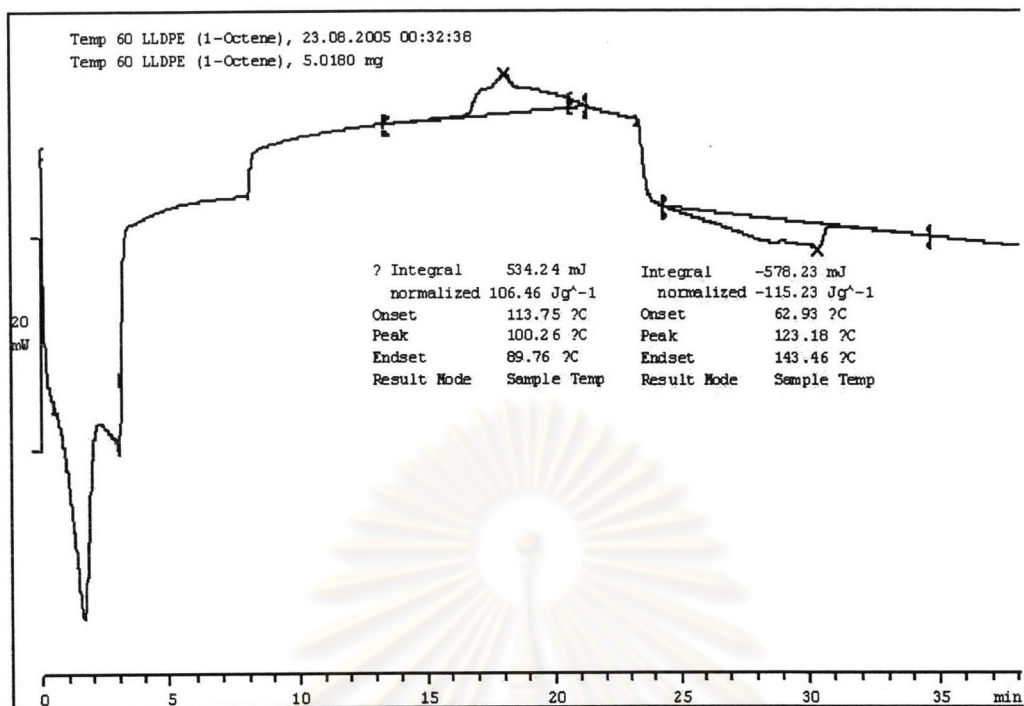




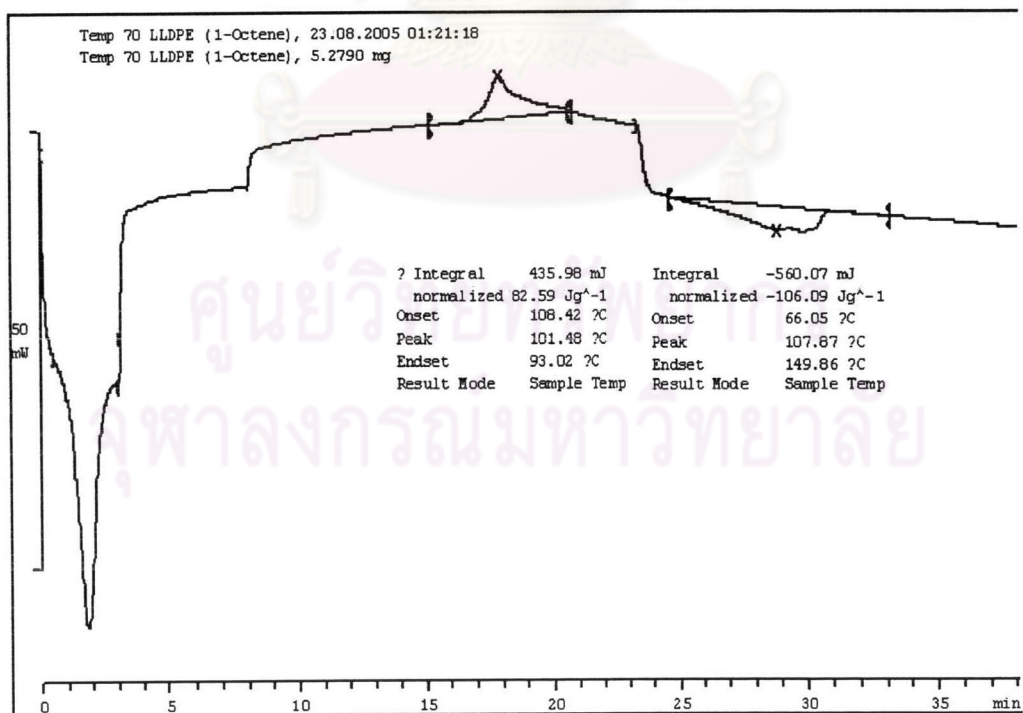
**Figure B.25** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 40°C.



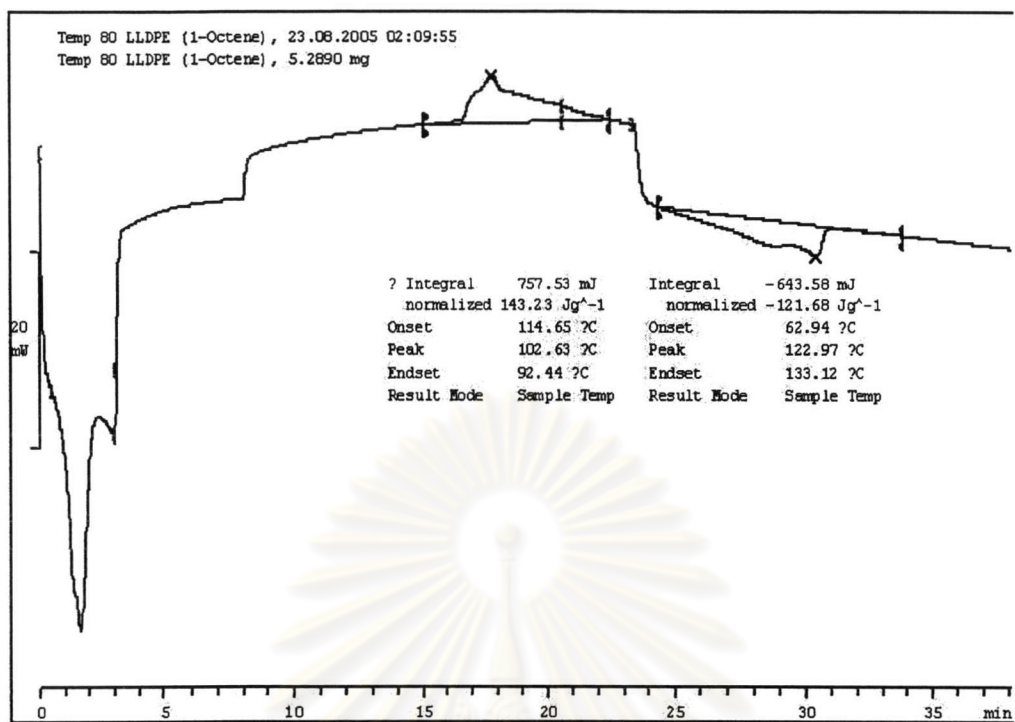
**Figure B.26** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 50°C.



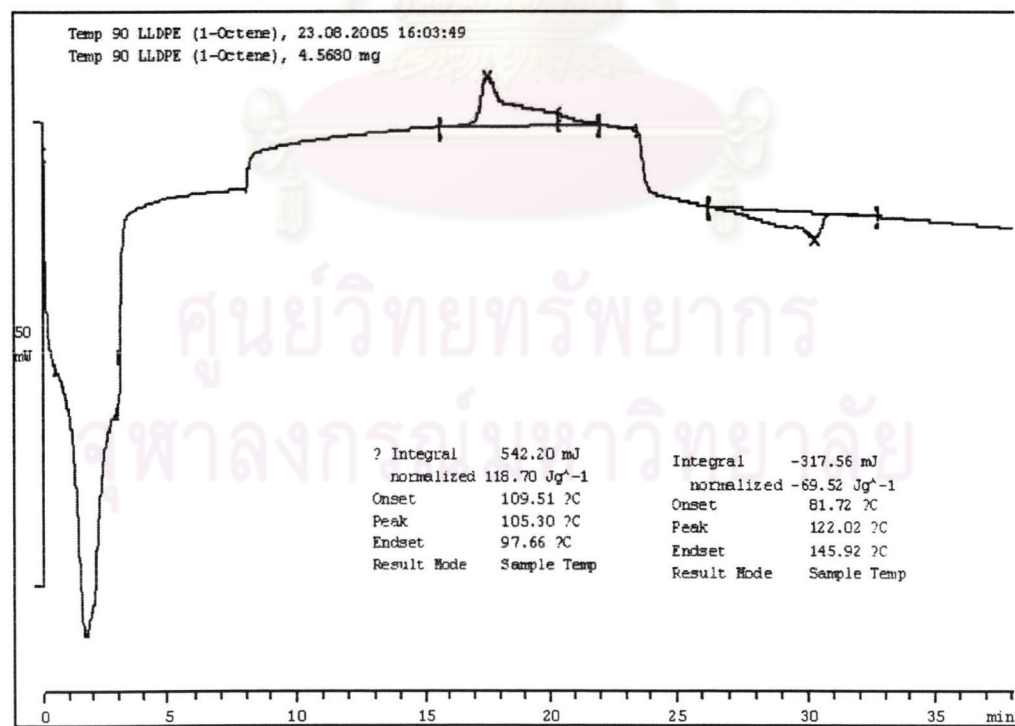
**Figure B.27** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 60°C.



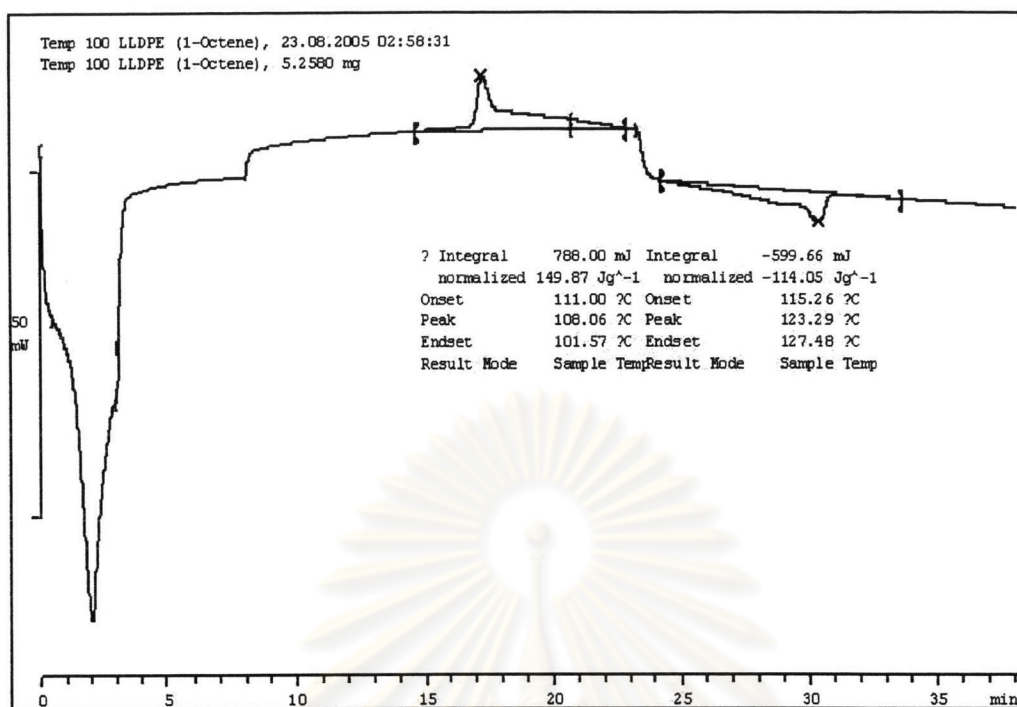
**Figure B.28** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 70°C.



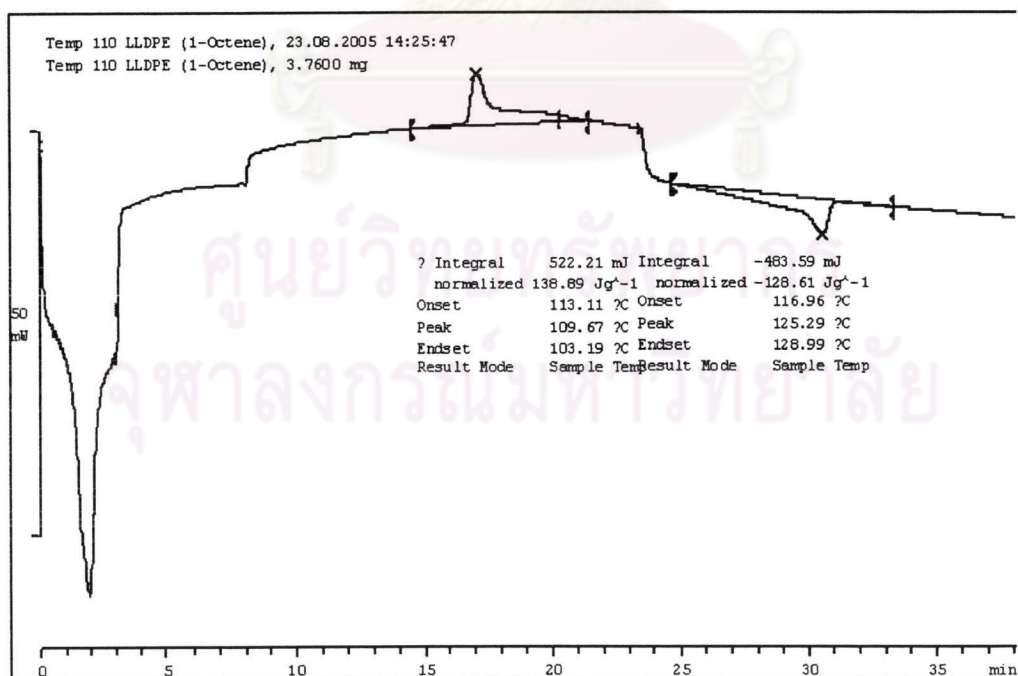
**Figure B.29** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 80°C.



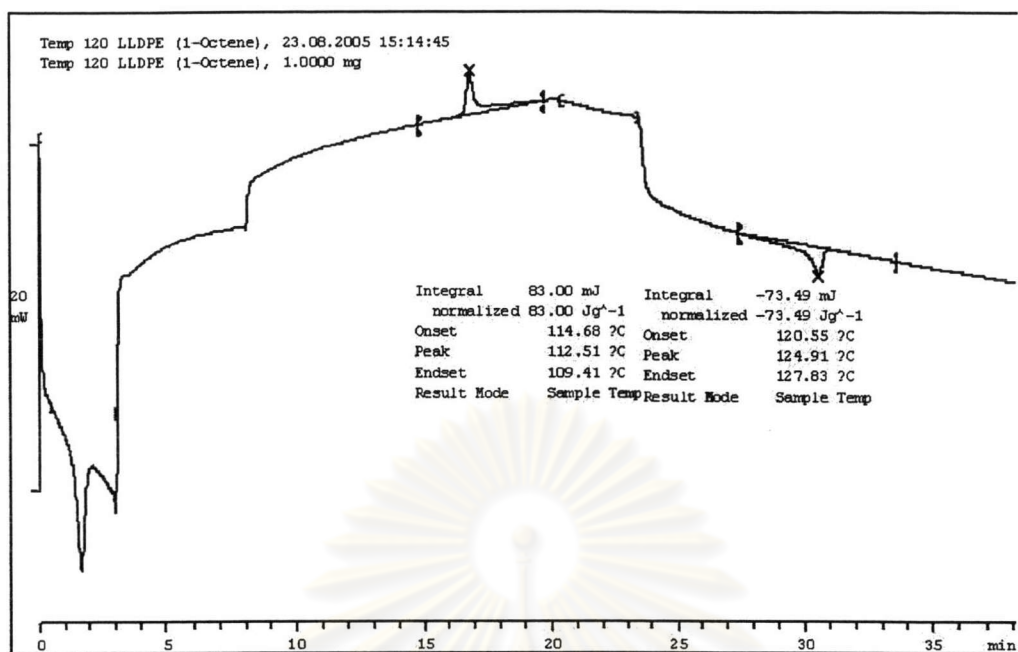
**Figure B.30** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 90°C.



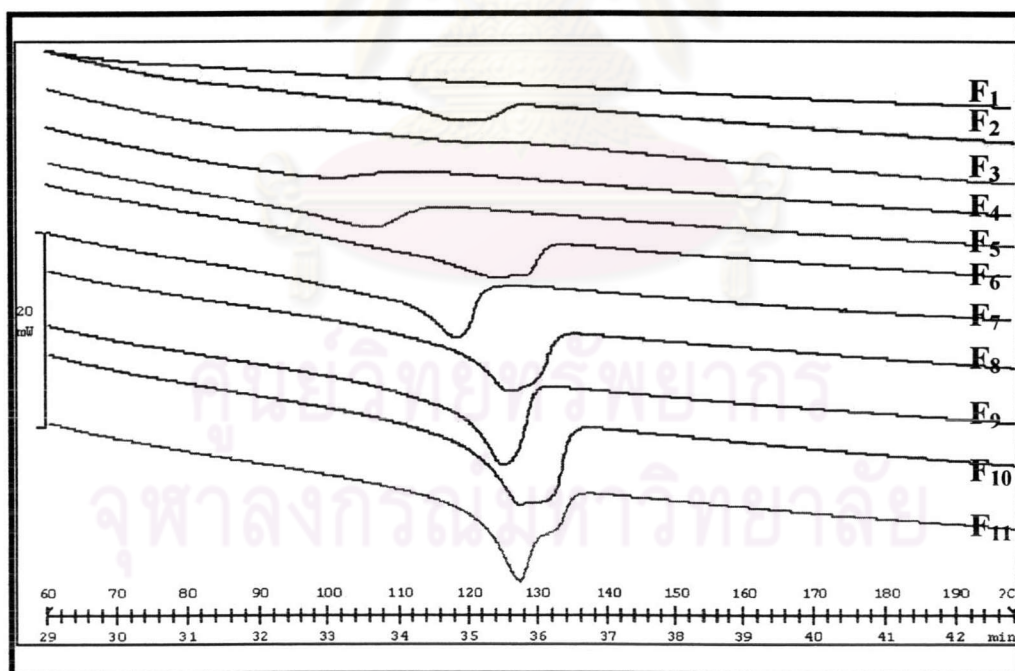
**Figure B.31** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 100°C.



**Figure B.32** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 110°C.

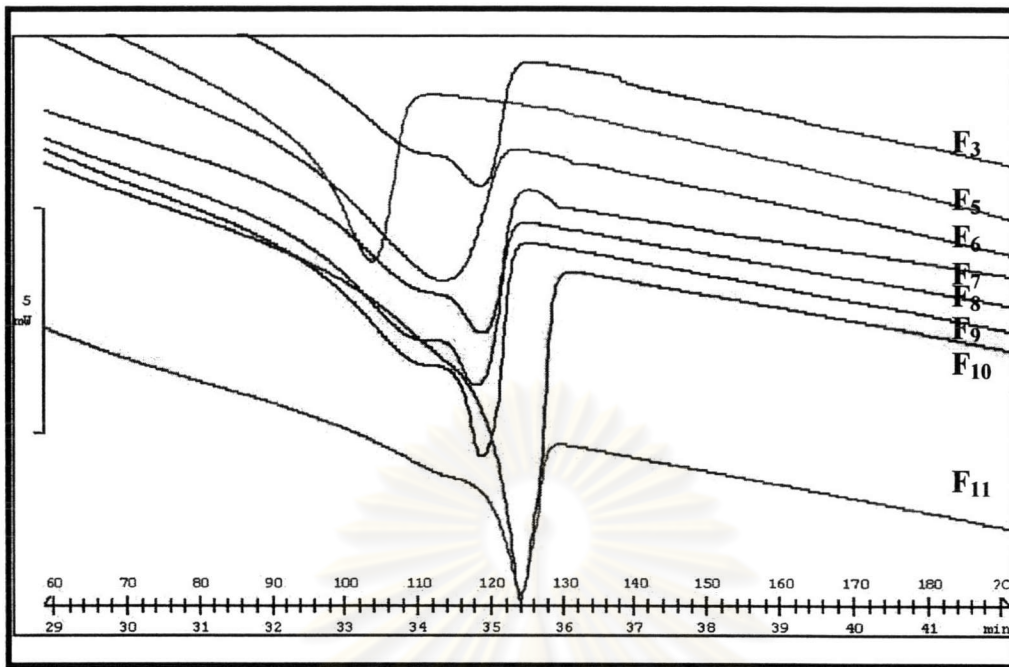


**Figure B.33** DSC thermogram on heating curve of fractionated C<sub>8</sub>-LLDPE at elution temperature 120°C.

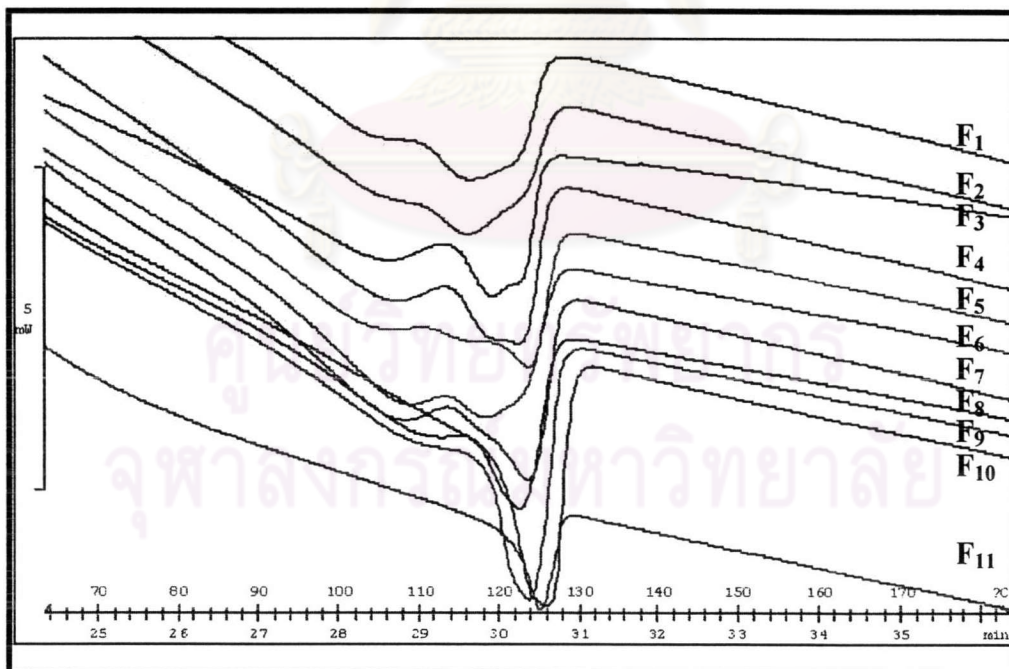


**Figure B.34** DSC thermograms on heating curve of fractionated C<sub>4</sub>-LLDPE (F1 to F11; elution temperature 20 to 120 °C).





**Figure B.35** DSC thermograms on heating curve of fractionated C<sub>6</sub>-LLDPE (F3, F5, F6, F7, F8, F9, F10, and F11; elution temperature 40, 60, 70, 80, 90, 100, 110 and 120°C).



**Figure B.36** DSC thermograms on heating curve of fractionated C<sub>8</sub>-LLDPE (F1 to F11; elution temperature 20 to 120 °C).



**APPENDIX C**

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

Table C-1 Molecular weight of whole polymer

Sample	Density (g/cm <sup>3</sup> )	M <sub>n</sub>	PDI
a: C <sub>4</sub> -LLDPE	0.918	29,184	3.53
b: C <sub>6</sub> -LLDPE	-	11,507	6.61
c: C <sub>8</sub> -LLDPE	-	8,052	6.41

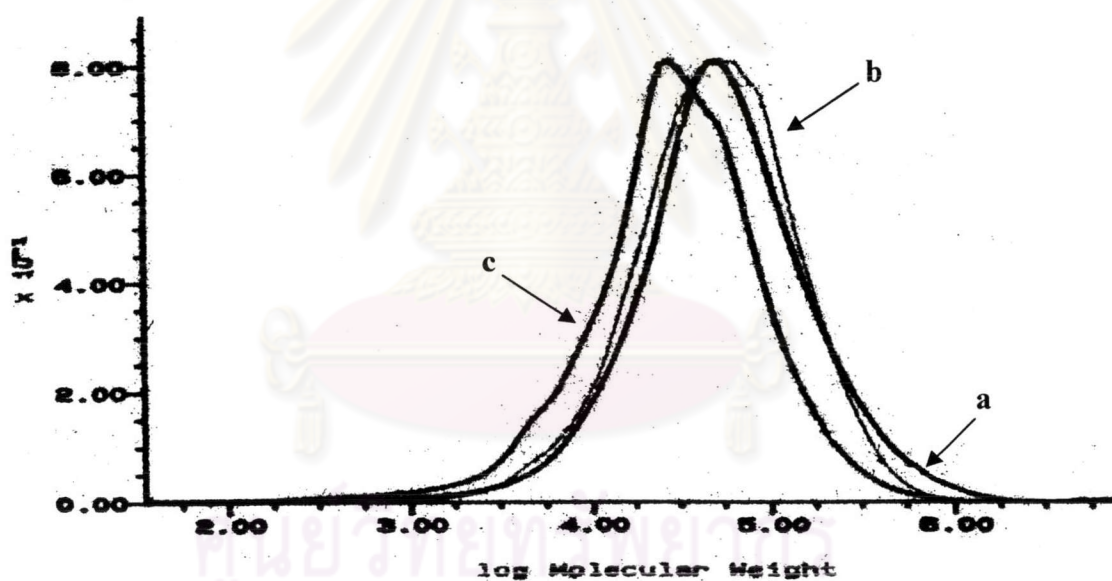
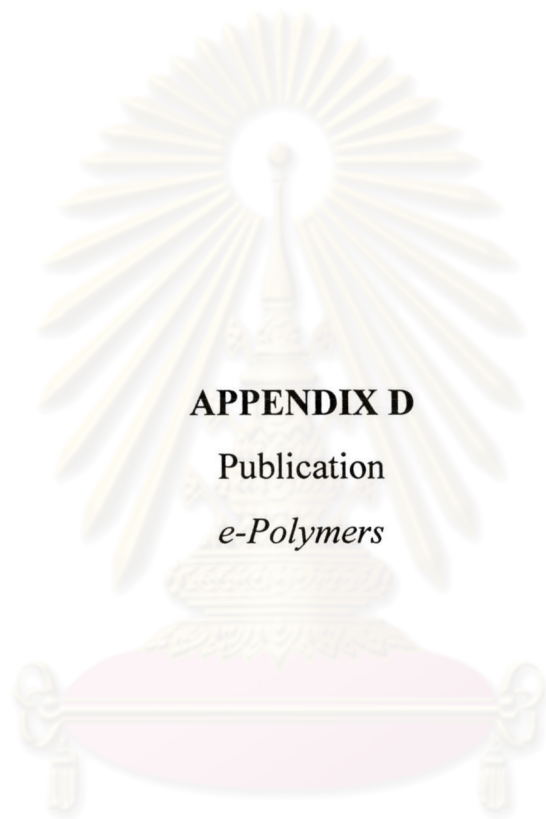


Figure C-1 Molecular weight distributions of whole polymer (a) C<sub>4</sub>-LLDPE, (b) C<sub>6</sub>-LLDPE and (c) C<sub>8</sub>-LLDPE.



**APPENDIX D**

Publication

*e-Polymers*

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



# Polyethylene Fractionation by Modified Temperature Rising Elution Fractionation Technique

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## Abstract

Though Temperature Rising Elution Fractionation (TREF) has been known as the most effective method for polyolefin fractionation, such as PE and PP. These polymers are semicrystalline and show various degrees of branching distribution which affects on their solubility. Unfortunately the drawback of preparative TREF is time-consuming, particularly, in the crystallization step. To solve this problem, mixed solvent for crystallization has been attempted. LLDPE resins produced commercially from ethylene and various comonomer such as 1-butene, 1-hexene and 1-octene were used in this study. It was found that the total analysis time depended on the strength of solvent used in the crystallization step.

**Keywords:** Short chain branching distribution, Polyethylene, TREF, Ethylene/ $\alpha$ -olefin copolymers

## 1. Introduction

Currently, linear low density polyethylene (LLDPE) is one of the most widely produced polymers in the world. The applications of LLDPE resins are very diverse and various LLDPE types are in use. The diversity of LLDPE types is a result of large variations in molecular structure such as molecular weight distribution (MWD), the average molecular weight and short chain branching distribution (SCBD). Especially, short chain branching [1-3] in the structure of LLDPE affects many physical and mechanical properties [4,5] such as rigidity density hardness permeability tensile strength and storage-loss moduli. To determine the compositional heterogeneity for polyolefins, Temperature Rising Elution Fractionation (TREF) is the most efficient technique [6-8]. Generally, TREF is composed of two sequential steps, namely crystallization and elution [7].

In the first step, the polymer is dissolved in a suitable solvent and then put in contact with an inert support. The crystallization is carried out under well controlled condition by slowly decreasing the temperature. In the elution step, solvent flows through a column packed with polymer coated inert support while the temperature is raised stepwise at an interval. Recently, many researchers used the preparative TREF and <sup>13</sup>C-NMR to determine short chain branching density of ethylene/ $\alpha$ -olefin copolymers. Since the cooling rate was mostly about 1.0-2.0 °C/h, the crystallization time became very time-consuming and a waste of energy [6, 7].

In the present study, we used preparative TREF as a primary technique to separate the polyethylene into different fractions with respect to their different crystallizability and combined multiple techniques to achieve the understanding of polymer structure and property relationships. To our knowledge these modified TREF methods have never been studied in literature. The aim of the present work was to carry

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out the comparative study of the mixed solvent used in the crystallization step and to solve the problem of time-consuming.

## 2. Materials and Methods

Three ethylene/ $\alpha$ -olefins copolymers, A B and C were used in this investigation. All samples were produced with multiple site catalysts; therefore, Chemical composition distribution was expected to be unnarrow and unimodal. For LLDPE(1-hexene) and LLDPE(1-octene) samples ,their polydispersity index (PDI) were close to 7. Table 1 summarizes the properties of the samples used in this experimental.

**Table 1** LLDPE Sample Data

Sample	Co-monomer	Density (g/cm <sup>3</sup> )	M <sub>n</sub>	PDI
A	1-butene	0.918	29,184	3.53
B	1-hexene	-	11,507	6.61
C	1-octene	-	8,052	6.41

## Experimental

### Temperature rising elution fractionation (TREF)

TREF analysis was carried out with the home-made preparative TREF apparatus. The preparative TREF was proceeded by a process of crystallization which involved the dissolution of polyethylene about 1 g with *o*-xylene , stabilized with Irganox 1010 which was previously stirred for 1 hour at 120 °C. Pouring into the column which loaded via glass beads (15.0 g) preheated at 120 °C and cooled down to 20 °C at a constant rate of 1, 5 and 10 °C/h respectively. The column was heated incremental step and eluted with *o*-xylene. At each step, the elution temperature slowly increased for a period of 1 hour and then remained constant for several hours until the peak of the specimen disappeared in the refractive index detector. The polymers of each fraction were precipitated with the addition of an excess volume of methanol or acetone while stirring. Filtered, dried at 80 °C over a period of 6 h and weighed. In the modified TREF, the mixed solvent used were ethylene glycol (EG) and *o*-xylene stabilized with Irganox 1010.

### Gel permeation chromatography (GPC)

Water 150 C, high temperature size exclusion chromatography, used to determine the molecular weight and with three linear mixed Shodex AT-806MS columns and a differential refractive index detector at 135 °C. The 1,2,4-trichlorobenzene (TCB) was used as the solvent at a flow rate of 1.0 ml/min. The universal calibration was carried out using monodisperse polystyrene standards.

### Differential scanning calorimeter (DSC)

Melting endotherms and of whole polymers and their fractions were determined using a METTLER. The samples were heated from 50 to 200 °C at 10 °C/min.

To take into account the thermal history of the samples used for the melting point and crystallinity were estimated

### <sup>13</sup>C-Nuclear magnetic resonance (<sup>13</sup>C-NMR)

This study use <sup>13</sup>C-NMR to characterize whole polymers and their fractions. Spectra were obtained with a Jeol JNM-A 500 MHz NMR spectrometer in TCB/deuterated *o*-dichlorobenzene at 120 °C and were used for the determination of copolymer compositions. The acquisition parameters and procedure, the chemical shift assignments of polymer chains and the calculations of copolymer compositions followed ASTM D 5017-91 method [9].

## 3. Results and Discussion

### Fractionation

The copolymers sample used in preparative TREF have relatively data. A comparison of the corresponding molecular weight distributions is shown in Fig. 1. The MWDs of the three resins are quite similar. The number average molecular weights ( M<sub>n</sub> ) of these samples are listed in Table 1. However their polydispersity (PD) indices do vary due to short chain branching in the high molecular weight region. The compositional distribution of the whole polymer is expressed in one way; the short chain branching content obtained from the preparative TREF profile by combining nuclear magnetic resonance and differential scanning calorimeter. Seven fractions for LLDPE (1-butene) were collected by TREF as show in Fig. 6. Their relative weight fractions were determined using the GPC technique. Fig. 3 give the DSC thermogram on heating curve of each whole resins. Fig. 4 give the DSC thermogram on heating curve of each fraction of LLDPE(1-butene) when used the single solvent in the crystallization step.

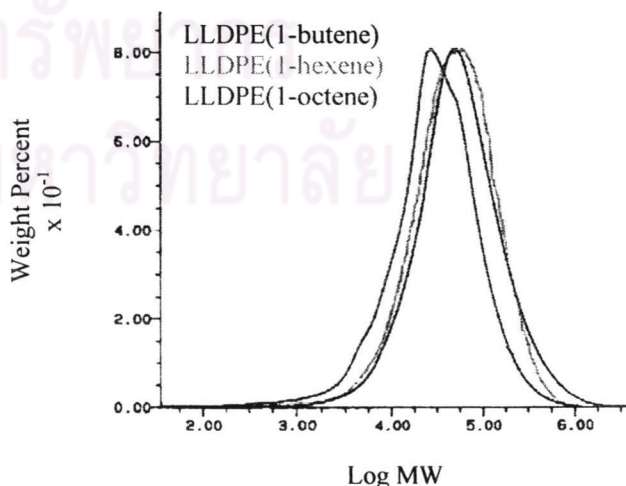


Fig. 1: Comparison of MWDs of each LLDPEs

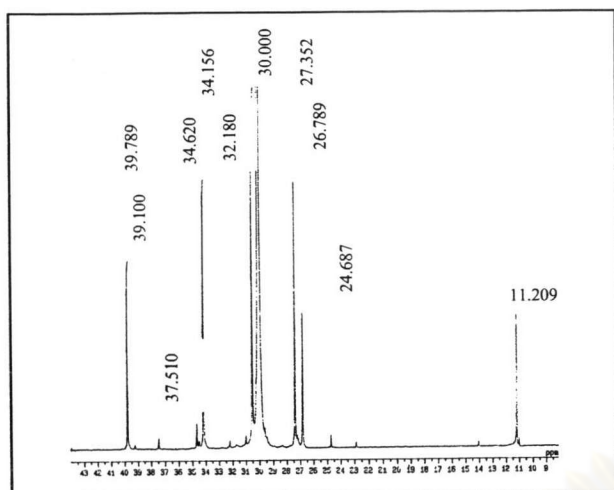


Fig. 2:  $^{13}\text{C}$ -NMR spectrum of LLDPE (1-butene) copolymers (whole resins)

Fig. 5 gives the DSC thermogram on heating curve of each fraction of LLDPE (1-butene) when used the mixed solvent. From the both figure showed that the fractionation are not different significantly. On the other hand the rates of crystallization are different. As preparative TREF elution temperature increased, the melting peak became sharper and the melting curve shifted toward high temperature. These results indicate that the increase in short chain branching content considerably diminished the melting temperature. Thus the short chain branching content is a dominant factor affecting the lamellar morphology and hence the melting and crystallization behaviors of ethylene/ $\alpha$ -olefin copolymers. Hence this study focuses on the effects of compositional structure on the melting and crystallization behavior.

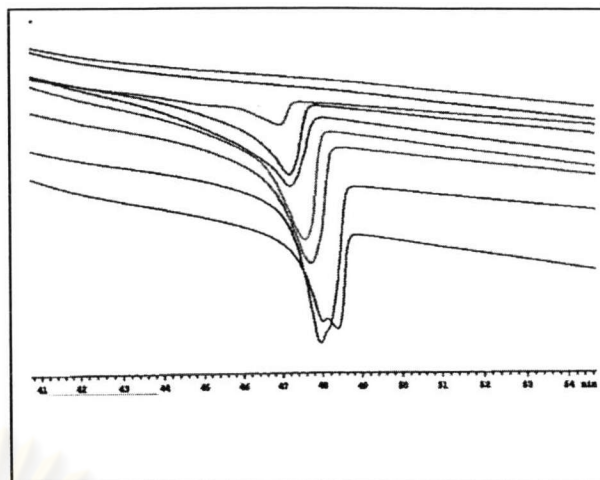


Fig. 4: DSC thermogram of each fraction of Sample A (single solvent)

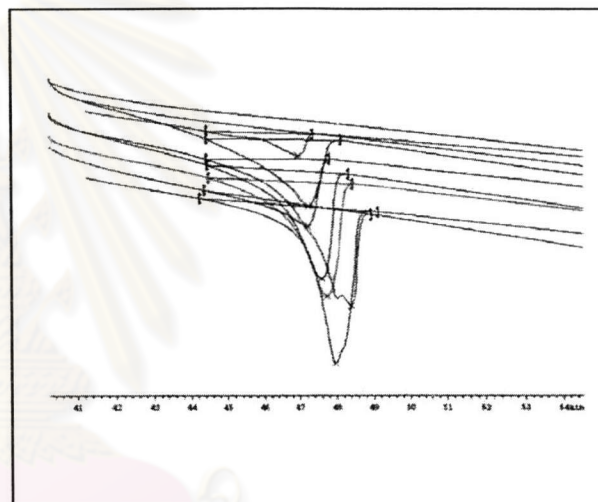


Fig. 5: DSC thermogram of each fraction of Sample A (mixed solvent)

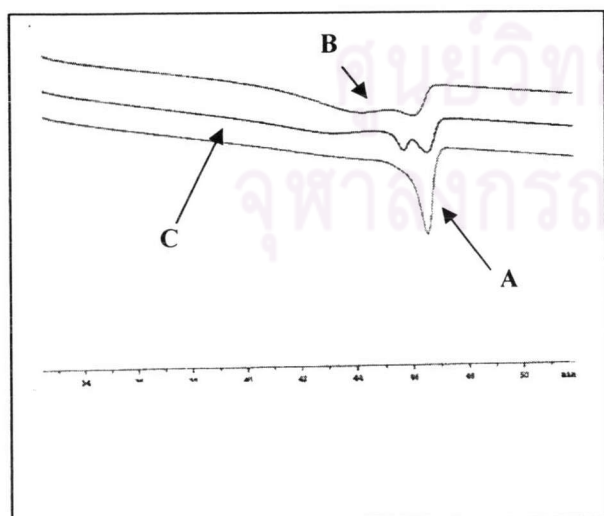


Fig. 3: DSC thermogram of A) LLDPE (1-butene), B) LLDPE (1-hexene), and C) LLDPE (1-octene).

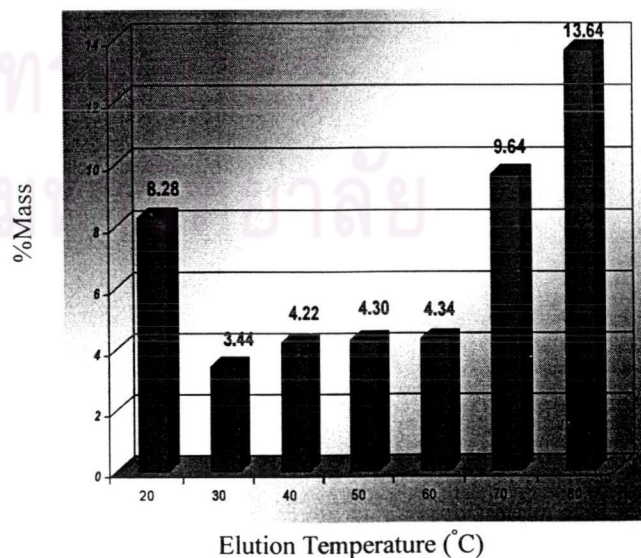


Fig. 6: Chemical composition distribution profile of LLDPE(1-butene)



#### 4. Conclusion

The crystallization step in TREF was improved by employing EG/xylene mixed system and faster cooling rate to reduce the fractionation time. Parameters that affect the fractionation are cooling rate, solvent for crystallization, and structure of polymer sample. Too fast cooling rate will give less time for crystallization. The polymer with higher chain branching content spends longer time in the solution than the one with lower chain branching content. From TREF and  $^{13}\text{C}$ -NMR results, short chain branching contents of every polymer fraction can be identified. This finding is useful for understanding and interpreting the physical and mechanical behavior of the whole polymer sample.

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## VITA

Mr. Nattawood Samoth was born on April 11, 1980 in Lop buri. He received the B. Sc.Degree in Chemistry Science at Kasetsart University in 2003. Since then, he has been a graduate student studying in the program of Petrochemistry and Polymer Science at Faculty of Science, Chulalongkorn University. He complete his MS in 2006.



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