CHAPTER IV

RESULTS AND DISCUSSION

4.1 Operational testing of preparative TREF apparatus

Since preparative TREF apparatus was set up in-house, the experiment condition at 1°C/h was a control parameter. In order to observe the reproducibility, the experiment of LLDPE samples was performed three times for each one. A 0.5 g of each sample: C_4-LLDPE, C_6-LLDPE and C_8-LLDPE, was completely dissolved in 30 ml of hot xylene as a proper solvent containing 0.1% of antioxidant, Irganox 1010. Whereas the polymer solution was cooled down from 120°C to 20°C with rate 1°C/h, the polymer fraction was crystallized on the glass bead as an inert support. When the temperature was stable at 20°C for 30 min, the temperature was raised up from 20°C to 120°C with rate 10°C/h stepwise. Then the fractionated polymer was collected at 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, and 120°C, respectively. The collected polymer was dried and weighed. Their results were shown as Table 4.1.

Table 4.1 Weight percent mean of LLDPEs at various elution temperature with cooling rate of 1°C/h

Sample	Elution temp (°C)	Experimental set			Mean	SD	RSD (%)
		1	2	3			
a) C_4-LLDPE							
	20	10.95	9.65	10.54	10.38	0.92	8.86
	30	6.72	5.93	6.23	6.29	0.56	8.88
	40	3.41	3.22	3.35	3.33	0.13	4.04
	50	3.95	3.56	3.23	3.58	0.28	7.70
	60	3.89	4.55	6.30	4.91	0.47	9.50
	70	14.96	16.34	16.40	15.90	0.98	6.14
	80	15.69	16.82	16.80	16.44	0.80	4.86
	90	13.60	14.25	12.54	13.46	0.46	3.41
	100	18.92	18.47	17.87	18.42	0.32	1.73
	110	5.29	4.88	4.56	4.91	0.29	5.90
	120	2.62	2.33	2.18	2.38	0.21	8.63
b) C_6-LLDPE							
	20	0.00	0.00	0.00	0.00	0.00	0.00
	30	0.00	0.00	0.00	0.00	0.00	0.00
	40	8.71	7.93	8.31	8.32	0.55	6.63
	50	1.69	1.54	1.48	1.57	0.11	6.76
	60	4.68	4.42	4.08	4.39	0.18	4.18
	70	9.93	8.97	9.53	9.48	0.68	7.16
	80	21.28	23.05	21.13	21.82	1.25	5.74
	90	15.30	14.87	15.64	15.27	0.30	1.99
	100	33.46	34.10	33.40	33.65	0.45	1.34
	110	3.61	3.90	4.63	4.05	0.21	5.07
	120	1.34	1.22	1.80	1.45	0.08	5.84
c) C_8-LLDPE							
	20	5.32	4.92	5.12	5.12	0.28	5.52
	30	6.47	5.81	6.17	6.15	0.47	7.59
	40	3.42	3.82	3.87	3.70	0.28	7.64
	50	11.00	10.94	10.87	10.94	0.04	0.39
	60	5.01	4.92	3.95	4.63	0.06	1.38
	70	12.23	12.94	14.30	13.16	0.50	3.82
	80	6.83	6.70	6.41	6.65	0.09	1.38
	90	22.88	23.78	21.25	22.64	0.64	2.81
	100	11.80	11.73	12.40	11.98	0.05	0.41
	110	13.69	12.90	13.48	13.36	0.56	4.18
	120	1.35	1.54	2.18	1.69	0.13	7.95

From the above results, it was founded that the RSD of weight fraction of each samples was less than 10%. It meant that the reproducibility of weight fraction value was accepted at the 90% confidence level. Moreover, the elution temperatures of

majors fraction of C_4-LLDPE, C_6-LLDPE and C_8-LLDPE were 100°C, 100°C, and 90°C, respectively. When each major fraction sample was investigated its melting temperature by means of DSC (see in Appendix B), it was close to the melting temperature of a whole sample of each one. It could be concluded that major fraction was a bulk property of polymer sample.

4.2 Branching content by means of ^{13}C-NMR spectroscopy

In order to analyze the branching content analysis, the fractionated polymer of each elution temperature was analyzed by means of high temperature ^{13}C-NMR spectroscopy in TCB/deuterated *o*-dichlorobenzene at 130°C. The key fraction of each sample was analyzed their branching content. The experiment of each sample was repeated three times. The results were displayed in Table 4.2. For the ^{13}C-NMR spectra and integration data were shown as Appendix A.3. The ^{13}C-NMR spectra were used for the determination of copolymer compositions according to ASTM D 5017-91 method [49].

Table 4.2 Branching content mean of LLDPEs at various elution temperature with cooling rate of 1°C/h

a) C_4-LLDPE

Elution temperature (°C)	Experimental set			Mean	SD	RSD (%)
	1	2	3			
30	7.918	7.908	7.915	7.914	0.005	0.06
60	4.524	4.529	4.526	4.526	0.002	0.04
70	3.231	3.224	3.222	3.226	0.005	0.15
80	2.388	2.390	2.397	2.392	0.005	0.21
90	1.545	1.563	1.550	1.553	0.009	0.58
100	1.609	1.606	1.589	1.601	0.011	0.69

b) C_6-LLDPE

Elution temperature (°C)	Experimental set			Mean	SD	RSD (%)
	1	2	3			
40	6.121	6.137	6.121	6.127	0.009	0.15
70	5.584	5.584	5.584	5.584	0.000	0.00
80	5.662	5.652	5.652	5.656	0.006	0.11
90	5.056	5.047	5.049	5.050	0.005	0.10
100	4.641	4.641	4.641	4.641	0.000	0.00

c) C_8-LLDPE

Elution temperature (°C)	Experimental set			Mean	SD	RSD (%)
	1	2	3			
20	6.644	6.652	6.630	6.642	0.011	0.17
30	5.724	5.726	5.735	5.729	0.006	0.10
50	4.616	4.521	4.519	4.552	0.055	1.21
70	3.887	3.879	3.854	3.873	0.017	0.44
80	3.379	3.394	3.394	3.389	0.009	0.27
90	2.988	2.988	2.989	2.989	0.001	0.03
100	2.604	2.616	2.618	2.613	0.007	0.27
110	2.475	2.472	2.475	2.474	0.002	0.08

From the above table, it was shown that the RSD of each sample was less than 10%. It meant that the reproducibility of branching analysis was acceptable at 90% confidence level, significantly. When elution temperature was increased, branching content was decreased. It obey the TREF concept that the first fraction is least crystalline or the longest branching. Then the more crystalline will be fractionated after at higher elution temperature. In addition, the branching content of fractionated polymer was cover on the branching content of a whole polymer sample.

4.3 Crystallization of LLDPE by using xylene as a single solvent

Since the drawback of TREF technique has been time consuming especially crystallization step, to solve this problem not only the cooling rate of crystallization step but also the mixed solvent system was investigated. In case of the cooling rate, it will directly effect on the analysis time for TREF technique. To find the maximum cooling rate of xylene as a single system, the cooling rates of both at 1°C/h as a control parameter and 5°C/h were observed. Moreover, the parameter of polymer type such as C_4-LLDPE, C_6-LLDPE and C_8-LLDPE was also investigated. Their results were discussed as following.

4.3.1 C₄-LLDPE

C$_4$-LLDPE was completely dissolved in hot xylene and held at 120°C, for 0.5 h. Thus it was crystallized from 120°C to 20°C with cooling rate 1, 3, 5, 7, 8 and 10°C/h. When the polymer crystallization was done, it was eluted by using xylene from 20°C to 120°C. Their results were displayed in Table 4.3.

Table 4.3 Branching content and weight percent of C$_4$-LLDPE at various cooling rates using single solvent system

Elution temperature (°C)	Cooling rate (°C/h)					
	1		3		5	
	Branching*	wt%	Branching*	wt%	Branching*	wt%
30	7.914	6.29	7.926	5.59	7.901	4.43
60	4.526	4.91	4.524	8.25	4.521	10.63
70	3.226	15.90	3.238	17.28	3.215	19.97
80	2.392	16.44	2.394	16.32	2.403	20.50
100	1.601	18.42	1.587	18.91	1.575	20.43
Elution temperature (°C)	7		8		10	
	Branching*	wt%	Branching*	wt%	Branching*	wt%
30	7.835	3.39	7.809	1.63	7.811	0.75
60	4.508	13.55	4.488	15.26	4.393	17.35
70	3.612	21.49	3.521	23.17	3.500	22.98
80	2.510	22.56	2.498	26.28	2.537	25.28
100	1.634	15.54	1.630	12.20	1.629	10.43

*Branches per 1000 carbons

From the above results, it indicated that the results of branching content and percentage fractionated polymer among 1°C/h, 3°C/h, and 5°C/h were similar to each other. It meant that the cooling rate in crystallization step at 1°C/h, 3°C/h, and 5°C/h was not effect on the efficiency of polymer fraction. For determining the maximum cooling rate, the higher cooling rate i.e. 7°C/h, 8°C/h, and 10°C/h, respectively was studied. It was found that the branching content and the fractionated polymer operated at 7°C/h, 8°C/h, and 10°C/h were different from each other because of not sufficient time for crystallizing. It can be summarized that C$_4$-LLDPE can be crystallized from 1°C/h to 5°C/h without effect on both weight percent and branching content of each polymer fraction.

4.3.1.1 Correlation of weight fraction percent and melting temperature

The eleven fractions, F1 to F11; elution temperature 20 to 120°C, of C_4-LLDPE obtained from preparative TREF display a multiple melting endotherm and drop in melt temperature with increasing degree of branching. This effect of branch concentration on melt temperature of the major endotherm was observed as shown in Appendix B. It was indicated that all the DSC curves were not symmetric in the neighborhood of the maximum.

4.3.2 C_6-LLDPE

For determining the maximum cooling rate in crystallization step of C_6-LLDPE, the cooling rate was varied from 1°C/h to 5°C/h. Their results were shown in Table 4.4.

Table 4.4 Branching content and weight percent of C_6-LLDPE at various cooling rates using single solvent system

Elution temperature (°C)	Cooling rate (°C/h)							
	1		2		3		5	
	Branching*	wt%	Branching*	wt%	Branching*	wt%	Branching*	wt%
40	6.127	8.32	6.149	3.22	6.056	1.13	5.989	1.05
70	5.584	9.48	5.585	12.36	5.580	16.32	5.592	25.16
80	5.656	21.82	5.660	25.80	5.433	24.16	5.344	42.08
90	5.050	15.27	5.040	19.53	5.110	43.30	5.069	21.54
100	4.641	33.65	4.641	35.98	4.789	10.20	4.677	5.05

*Branches per 1000 carbons

From the above results, it was clearly indicated that branching content and of the fractionated polymer at 2°C/h was the same as at 1°C/h, the control parameter. However, at 3°C/h and at 5°C/h their branching contents were different from the control parameter. In order to test that the branching content differ from the control parameter or not, t-test method was used for doing this. It detail of this test was explained in Appendix A.4. It was found that the branching content of cooling rate at both 3°C/h and 5°C/h was accepted at 95% confidence level.

4.3.2.1 Correlation of weight fraction percent and melting temperature

The eight fractions (F3, F5, F6, F7, F8, F9, F10, and F11; elution temperature 40, 60, 70, 80, 90, 100, 110 and 120°C) of C_6-LLDPE obtained from preparative TREF display a multiple melting endotherm and drop in melt temperature with increasing degree of branching. This effect of branch concentration on melt temperature of the major endotherm was observed as shown in Appendix B. It was indicated that all the DSC curves were not symmetric in the neighborhood of the maximum.

4.3.3 C_8-LLDPE

On the same purpose as above, the cooling rate was varied from 1°C/h to 5°C/h. They were exhibited in Table 4.5.

Table 4.5 Branching content and weight percent of C_8-LLDPE at various cooling rates using single solvent system

Elution temperature (°C)	Cooling rate (°C/h)							
	1		2		3		5	
	Branching*	wt%	Branching*	wt%	Branching*	wt%	Branching*	wt%
20	6.642	5.12	6.615	3.34	6.532	1.20	6.418	0.84
30	5.729	6.15	5.731	5.22	5.642	3.20	5.210	1.93
50	4.552	10.94	4.679	7.14	4.938	7.36	4.492	15.21
70	3.873	13.16	3.831	15.40	3.937	19.23	3.924	21.02
80	3.389	6.65	3.368	11.60	3.423	13.25	3.431	13.40
90	2.989	22.64	2.980	25.90	3.008	22.43	3.289	15.16
100	2.613	11.98	2.597	12.80	2.640	9.84	2.642	7.53
110	2.474	13.36	2.471	7.80	2.479	5.69	2.434	3.23

*Branches per 1000 carbons

It was found that the branching content and weight percent of cooling rate at 1°C/h and 2°C/h were not different in t-test method. However, at 3°C/h and 5°C/h were different from both 1°C/h and 2°C/h, respectively.

4.3.3.1 Correlation of weight fraction percent and melting temperature

The eleven fractions (F1 to F11; elution temperature 20 to 120°C) of C$_8$-LLDPE obtained from preparative TREF display a multiple melting endotherm. This effect of branch concentration on melt temperature of the major endotherm was observed as shown in Appendix B. It was indicated that all the DSC curves were the same trend in C$_6$-LLDPE and C$_8$-LLDPE.

Summary

From the experiment (4.2.1), (4.2.2), and (4.2.3), it can be summarized that the cooling rate at 1°C/h was applied for all, C$_4$-LLDPE, C$_6$-LLDPE, and C$_8$-LLDPE. However, at 2°C/h could still operate for both C$_6$-LLDPE, and C$_8$-LLDPE. Whereas C$_4$-LLDPE could be operated not only 3°C/h but 5°C/h as well. When the curve was plotted between the weight percent versus elution temperature called TREF curves, the weight fraction curved of C$_4$-LLDPE, C$_6$-LLDPE, and C$_8$-LLDPE were expressed as Figure 4.1.
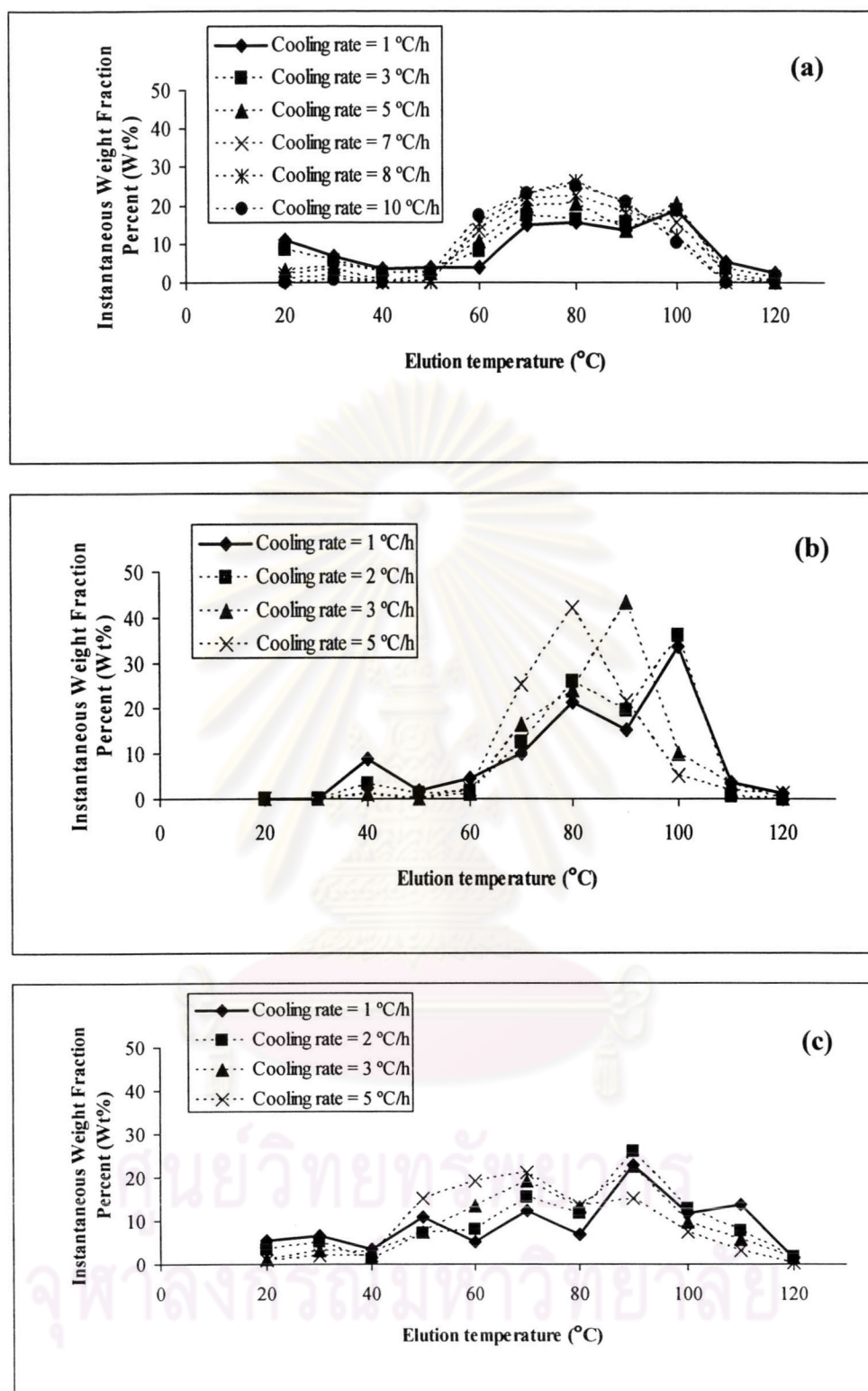
ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Figure 4.1 TREF curves of samples (a) C_4-LLDPE, (b) C_6-LLDPE, and (c) C_8-LLDPE at various cooling rate in the single solvent system (xylene).

From the weight fraction curve, it was found that when the cooling rate was increased, the weight percent was shifted. At low elution temperature its weight percent was lower [38]. On the other hands weight percent of higher elution temperature was higher accept major fraction. Even the higher branching of polymer like C_6-LLDPE and C_8-LLDPE was also the same trends because it was not sufficient time for crystallizing.

4.4 Crystallization of LLDPE by using mixed solvent

For increasing the cooling rate, the non-solvent like ethylene glycol (EG) and glycerol was mixed into xylene, a good solvent, for the three LLDPE samples. The detail is shown in the following.

4.4.1 Ethylene glycol (EG)/xylene

4.4.1.1 Determination of proper percentage of EG/xylene

The major fractions of three LLDPEs: C_4-LLDPE, C_6-LLDPE, and C_8-LLDPE, were used for this study.

Table 4.6 Weight percent of major fraction of LLDPEs

Major Fraction	Weight, %
C_4-LLDPE (Elution fraction at 100^oC)	18.42
C_6-LLDPE (Elution fraction at 100^oC)	33.65
C_8-LLDPE (Elution fraction at 90^oC)	22.64

Table 4.7 Weight percent of major fraction of LLDPEs at various %ethylene glycol/xylene

Sample	%Ethylene glycol/xylene					
	0	0.1	0.3	0.5	0.7	1
C_4-LLDPE	18.92	18.85	18.90	15.53	0.00	0.00
C_6-LLDPE	33.46	33.50	32.03	0.00	0.00	0.00
C_8-LLDPE	22.88	22.83	22.45	0.00	0.00	0.00

The ethylene glycol concentration was varied from 0.1% to 1.0%. At a higher EG concentration, homogeneous mixing between the two solvents could not be achieved. From Table 4.7, the weight percentage of major fraction of each polymer was not significantly changed when the EG concentration was increased to 0.3% in xylene. Moreover, at 0.5% the major fractions of C_6-LLDPE, and C_8-LLDPE were not observed. It is because the major fraction was precipitated at lower elution temperature. Therefore, it could be concluded that the appropriated concentration for crystallization of LLDPE copolymer sample was 0.3% EG/xylene.

4.4.1.2 Crystallization of LLDPE by using EG/xylene

In order to investigate the influence of cooling rate on LLDPE copolymers: C_4-LLDPE, C_6-LLDPE, and C_8-LLDPE, 0.3% EG/xylene was used as a medium for dissolving and crystallization. Then pure xylene was applied for eluting the crystallized polymer adsorbed on the beads. Both branching content and weight percent of all LLDPE copolymer were reported on detail as follows.

Table 4.8 Branching content and weight fraction of C_4-LLDPE at various cooling rates using 0.3%ethylene glycol/xylene

Elution temperature (°C)	Cooling rate (°C/h)					
	1		3		5	
	Branching*	wt%	Branching*	wt%	Branching*	wt%
30	7.902	4.69	7.910	3.21	7.910	2.32
60	4.521	11.20	4.528	15.50	4.532	18.70
70	3.216	15.40	3.224	17.71	3.236	20.40
80	2.381	17.20	2.401	15.60	2.398	19.80
100	1.589	17.98	1.614	18.49	1.605	16.20
Elution temperature (°C)	7		8		10	
	Branching*	wt%	Branching*	wt%	Branching*	wt%
30	7.927	3.20	7.937	1.43	8.124	1.75
60	4.532	16.22	4.543	19.26	4.603	21.35
70	3.236	22.10	3.345	23.40	3.392	25.98
80	2.400	21.70	2.413	24.28	2.468	26.28
100	1.618	16.80	1.628	12.30	1.632	9.82

*Branches per 1000 carbons

From Table 4.8, when using 0.3% EG/xylene both branching content and weight percent were not different from each other at the cooling rate from 1°C/h to 7°C/h. It was confirmed by t-test method shown in Appendix A. Moreover, the branching content of the fraction obtained from 7°C/h cooling rate was somewhat close to the ones from other cooling rates, except for the 8 and 10°C/h. Therefore the crystallization time could be decreased by using the mixed EG/xylene without losing fraction efficiency.

Table 4.9 Branching content and weight fraction of C_6-LLDPE at various cooling rates using 0.3%ethylene glycol/xylene

Elution temperature (°C)	Cooling rate (°C/h)							
	1		2		3		5	
	Branching*	wt%	Branching*	wt%	Branching*	wt%	Branching*	wt%
40	6.147	6.54	6.103	6.23	6.087	2.02	6.023	1.53
70	5.584	10.53	5.583	8.95	5.601	15.57	5.809	22.56
80	5.670	18.97	5.641	21.28	5.633	20.16	5.593	38.55
90	5.049	17.22	5.045	20.30	5.034	35.60	5.116	20.54
100	4.641	35.58	4.642	32.14	4.630	17.72	4.654	8.05

*Branches per 1000 carbons

From Table 4.9, it exhibited that the cooling rate of 1°C/h produced the fraction with the same branching content as that from the rate of 2°C/h. It can be concluded that the branching content of the fraction separated by the mixed solvent system was not different from the pure xylene.

Table 4.10 Branching content and weight fraction of C_8-LLDPE at various cooling rates using 0.3%ethylene glycol/xylene

Elution temperature (°C)	Cooling rate (°C/h)							
	1		2		3		5	
	Branching*	wt%	Branching*	wt%	Branching*	wt%	Branching*	wt%
20	6.625	6.40	6.580	3.03	6.563	2.85	6.500	1.43
30	5.740	7.17	5.688	3.51	5.700	3.24	5.751	2.18
50	4.672	9.05	4.701	11.80	4.712	15.60	4.723	18.32
70	3.907	11.50	3.823	16.30	3.814	18.23	3.802	21.02
80	3.408	7.41	3.412	13.20	3.425	15.20	3.430	13.40
90	2.990	21.53	3.097	21.32	2.994	18.90	3.010	15.16
100	2.630	13.40	2.641	7.80	2.638	5.54	2.654	7.53
110	2.478	12.15	2.485	7.12	2.492	5.66	2.498	3.23

*Branches per 1000 carbons

From Table 4.10, in order to test that the single solvent system was different from the mixed system or not. T-test method (in appendix A) was used. It was found that the single solvent system at 1°C/h as a control parameter was the same as the mixed solvent system.

Summary

The concentration of EG/xylene at 0.3% was suitable for fractionating the LLDPE copolymer like C_4-LLDPE, C_6-LLDPE, and C_8-LLDPE. For the influence of cooling rate on the fractionated polymer, it was concluded that the cooling rates at 1°C/h, 3°C/h, 5°C/h and 7°C/h could be applied for C_4-LLDPE. However, in case of both C_6-LLDPE and C_8-LLDPE, the suitable cooling rate was at 2°C/h and 1°C/h. Moreover, the effect of cooling rate on the weight fraction curve or TREF curve was shown as below figure 4.2. It was found that when the cooling rate was increased the weight fraction curve was shifted to the middle of curve. Furthermore, the shape of weight fraction curve of C_4-LLDPE was not changed at cooling rate from 1°C/h to 7°C/h. But the shape of C_6-LLDPE and C_8-LLDPE one was different from the cooling rate at 1°C/h as the original one. The reason of this phenomenon might be not sufficient time for depositing the crystalline of fractionated polymer on the inert support.
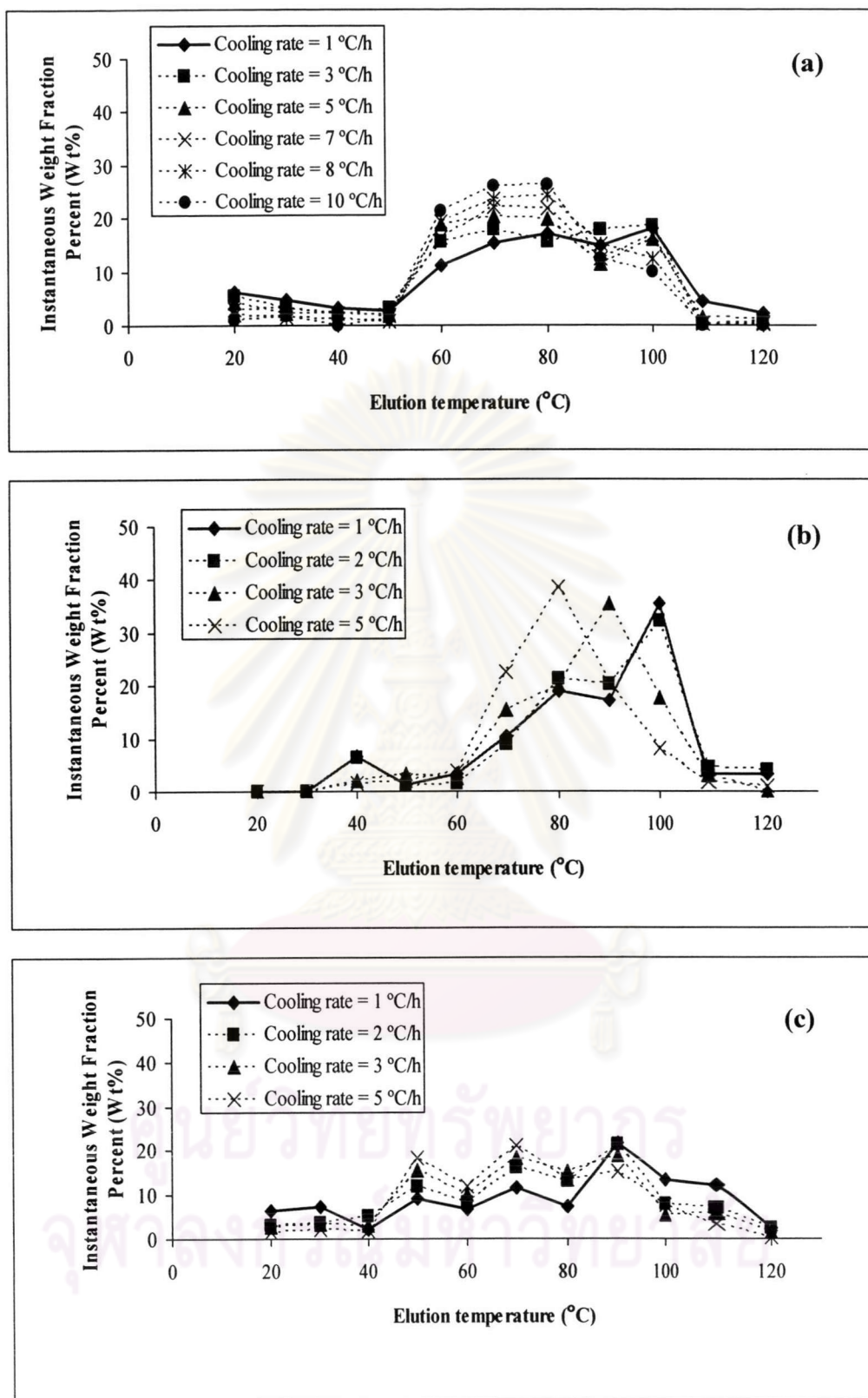
Figure 4.2 TREF curves of samples (a) C_4-LLDPE, (b) C_6-LLDPE, and (c) C_8-LLDPE at various cooling rate in the mixed solvent system (0.3%ethylene glycol/xylene).

4.4.2 Glycerol/xylene

4.4.2.1 Determination of proper percentage of glycerol/xylene

To determine the optimum concentration of glycerol/xylene, the glycerol concentration was varied from 0.1% to 1.0%. The condition for analysis was the same as the ethylene glycol/xylene system. Their results were shown in Table 4.11

Table 4.11 Weight percent of major fraction of LLDPEs at various % glycerol/xylene

Sample	% Glycerol/xylene					
	0	0.1	0.3	0.5	0.7	1
C_4-LLDPE	18.92	18.85	10.25	0.00	0.00	0.00
C_6-LLDPE	33.46	33.34	0.00	0.00	0.00	0.00
C_8-LLDPE	22.88	22.73	0.00	0.00	0.00	0.00

Only 0.1% glycerol/xylene system has produced the same amount of major fraction as pure xylene. was closed to pure xylene. It meant that the proper concentration of glycerol/xylene was 0.1%. Moreover, immisciblility between glycerol and xylene was observed when glycerol concentration was over 0.5%.

4.4.2.2 Crystallization of LLDPE by using glycerol/xylene

In order to investigate the effect of cooling rate on the fractionated polymer, 0.5 g of polymer sample was completely dissolved by using 0.1% glycerol/xylene at $120^{\circ}C/h$ for 0.5h. Then it was cooled down from $120^{\circ}C/h$ to $20^{\circ}C/h$ with varied cooling rate at $1^{\circ}C/h$ and $2^{\circ}C/h$, respectively. Both branching content and weight percent were reported.

Table 4.12 Branching content and weight fraction of C_4-LLDPE at various cooling rates using 0.1%glycerol/xylene

Elution temperature (°C)	Cooling rate (°C/h)			
	1		2	
	Branching*	wt%	Branching*	wt%
30	7.925	5.94	7.947	6.42
60	4.530	10.47	4.561	13.40
70	3.236	11.53	3.274	9.69
80	2.392	18.32	2.432	18.92
100	1.625	17.45	1.673	16.80

*Branches per 1000 carbons

It was found that the weight percents obtained from 1°C/h and 2°C/h were not different. However, the branching content at 2°C/h was different from that at 1°C/h. Therefore that glycerol could not be used to reduce the crystallization time.

Table 4.13 Branching content and weight fraction of C_6-LLDPE at various cooling rates using 0.1%glycerol/xylene

Elution temperature (°C)	Cooling rate (°C/h)			
	1		2	
	Branching*	wt%	Branching*	wt%
40	6.140	5.12	6.170	1.45
70	5.592	8.40	5.589	16.54
80	5.650	24.30	5.680	16.12
90	5.060	20.46	5.084	32.15
100	4.641	32.90	4.652	24.14

*Branches per 1000 carbons

In the case of C_6-LLDPE, the observed trend was similar to C_4-LLDPE.

Table 4.14 Branching content and weight fraction of C$_8$-LLDPE at various cooling rates using 0.1%glycerol/xylene

Elution temperature (°C)	Cooling rate (°C/h)			
	1		2	
	Branching*	wt%	Branching*	wt%
20	6.650	5.00	6.670	3.40
30	5.743	5.96	5.762	4.73
50	4.689	10.64	4.697	17.94
70	3.917	14.24	3.925	11.20
80	3.409	6.61	3.420	9.46
90	2.990	21.31	2.993	20.10
100	2.630	11.35	2.634	13.30
110	2.471	14.20	2.480	10.69

*Branches per 1000 carbons

For C$_8$-LLDPE the same result with C$_4$-LLDPE and C$_6$-LLDPE was obtained. It was because the polarity of glycerol was a much different from xylene. Therefore glycerol does not help improving the cooling rate but also causes the polymer to precipitate since glycerol is a non-solvent for LLDPE.

Summary

From the above results, it could be summarized that the cooling rate could not be improved by using 0.1% glycerol/xylene not only C$_4$-LLDPE but also C$_6$-LLDPE, and C$_8$-LLDPE. Especially, weight fraction curves or TREF curves were not changed. It was shown in Figure 4.3.

However, the branching content was exhibited that it was different. It meant that 0.1% glycerol could not improved the drawback of TREF.
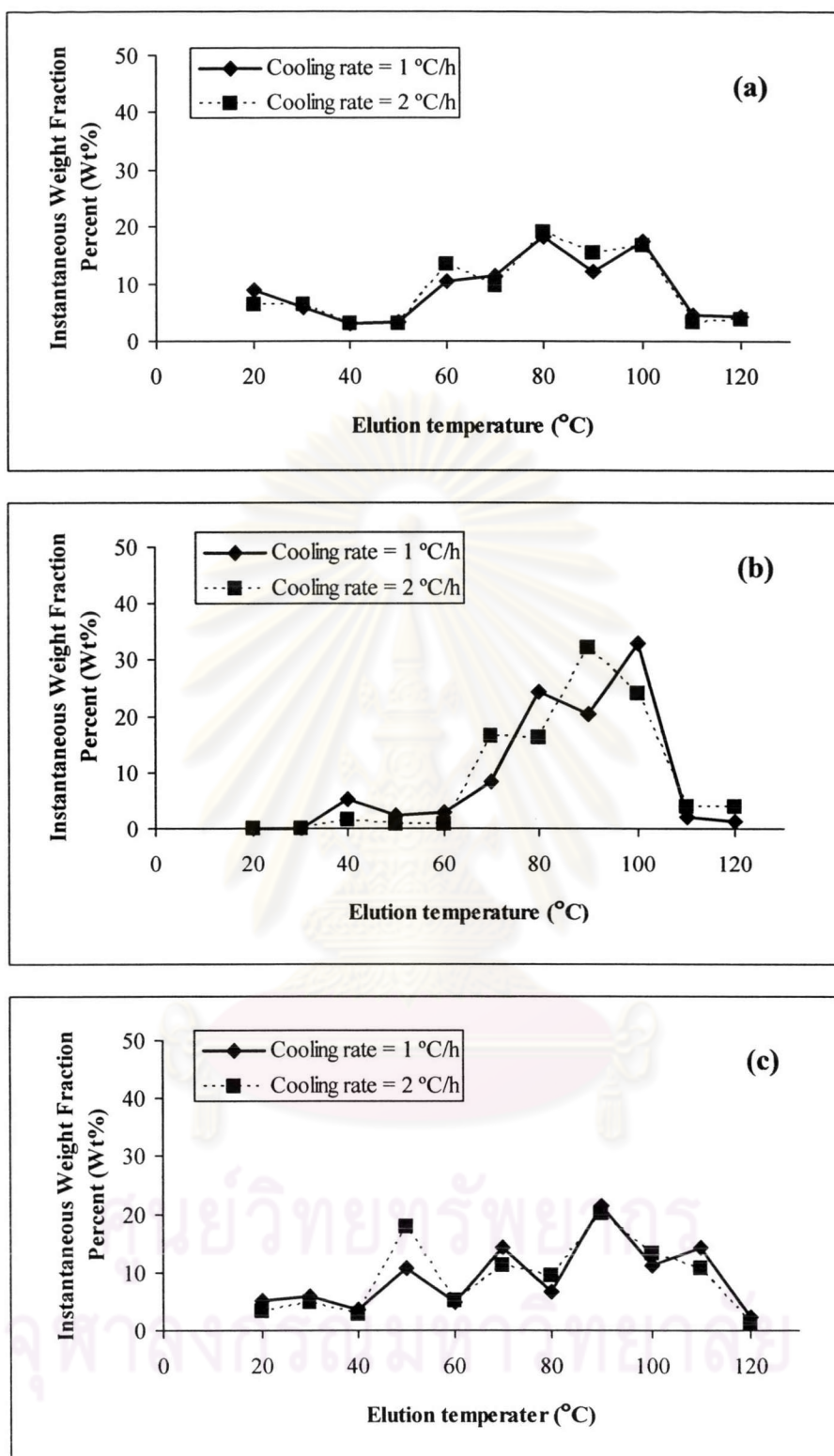
Figure 4.3 TREF curves of samples (a) C_4-LLDPE, (b) C_6-LLDPE, and (c) C_8-LLDPE at various cooling rate in the mixed solvent system (0.1%glycerol/xylene).