

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Polymerization of L-lactic acid

L-lactide synthesis was divided into two steps. The first step was to produce low molecular weight PLLA. In the second step, L-lactide was produced by ring formation by decomposition of low molecular weight PLLA [10, 31].

4.1.1 Synthesis of low molecular weight polylactide using toluene-4-sulfonic acid monohydrate (PTSA) as a catalyst.

L-lactic acid was heated with toluene-4-sulfonic acid monohydrate until temperature reached 100°C so that water present in L-lactic solution was removed and condensed into the condensate reservoir (Figure 4.1). The temperature was maintained at 100-115°C for 2-3 hours to remove water and by product. When temperature reached 140°C, the solution was changed from white clear liquid to very light yellow liquid. Later, the vacuum pressure was applied for 30 minutes to further remove of water from the reaction.

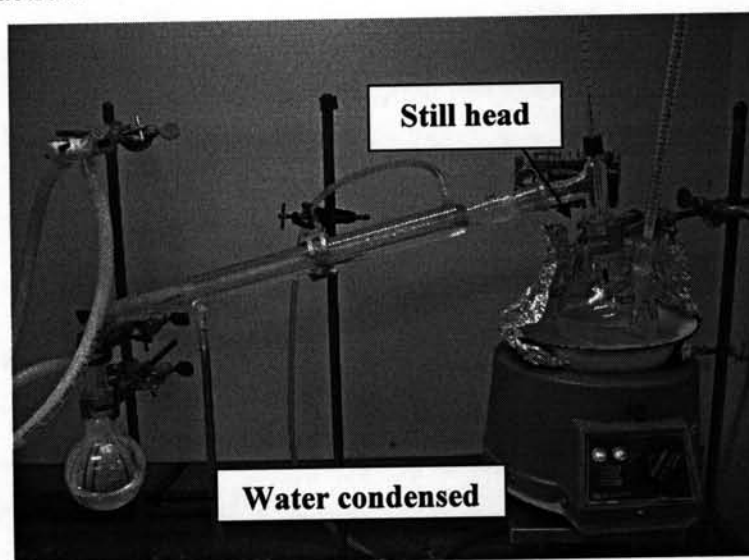


Figure 4.1 Experimental set up for low molecular weight PLLA synthesis.

4.1.2 Ring formation of L-lactide from low molecular weight polylactide using stannous 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) as a catalyst.

The $\text{Sn}(\text{Oct})_2$ was added into the light yellow liquid obtained in 4.1.1 and the reaction mixture was heated to 160°C for 30 minutes or until water was not condensed into the condensate reservoir. Then, the temperature was increased to $220\text{--}230^\circ\text{C}$ and the vacuum pressure was applied until white solid crystal of L-lactide was formed. The L-lactide crystal was purified by recrystallization.

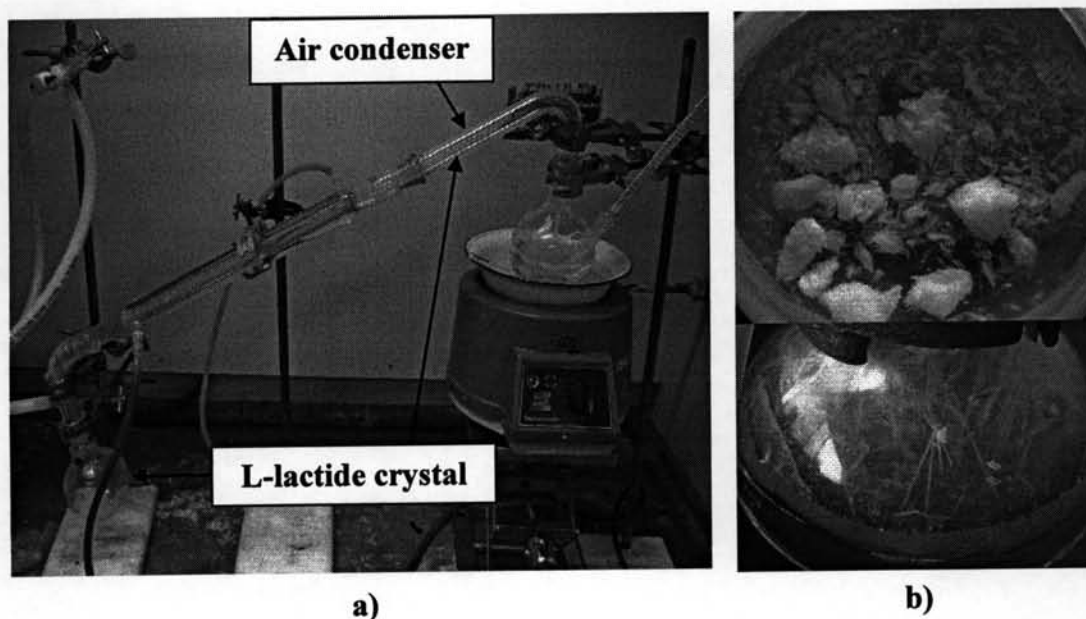


Figure 4.2 a) Experimental set up for L-lactide ring formation and b) L-lactide crystal

The L-lactide crystal was characterized by NMR technique. From ^1H NMR spectrum in Figure A-1, chemical shift at 5.07 ppm was assigned for $-\text{CHCH}_3$ group, and 1.66 ppm for $-\text{CHCH}_3$ group. Moreover, ^{13}C NMR spectrum in Figure A-2 indicated the peak at 169 ppm for $-\text{COO}$ group, 68 ppm for $-\text{COH}$ group, and 16 ppm for CH_3 group.

In Table 4.1, the different solubility of reactant and products was used for purification of the L-lactide crystal from L-lactic acid and contaminate. The L-lactide crystal was crystallized and separated from L-lactic acid monomer with cold ethyl acetate.

Table 4.1 Solubility of monomer or polymer prepared.

Monomer or polymer	Solubility			
	Cold EtOAc	CH ₂ Cl ₂	MeOH	H ₂ O
L-lactic acid	S	S	S	S
L-lactide	NS	S	S	S
Poly(L-lactide)	NS	S	NS	NS

S = Soluble and NS = Non-soluble

4.2 Polymerization of L-lactide

L-lactide crystal was recrystallized in ethyl acetate before used. The L-lactide crystal 2.0 g and catalyst 0.006 g (weight ratio of initiator to L-lactide is 0.3:100) were placed in 25 ml round bottom flask and nitrogen gas was flew for 5 minutes before covering with nitrogen balloon. The round bottom flask was heated in silicone oil bath. Tin(II) 2-ethylhexanoate [32-34] and creatine hydrate were used as initiators in this polymerization reaction.

From Table 4.1, PLLA was purified from L-lactide monomer and oligomer by dissolved in methylene chloride and precipitated with excess methanol.

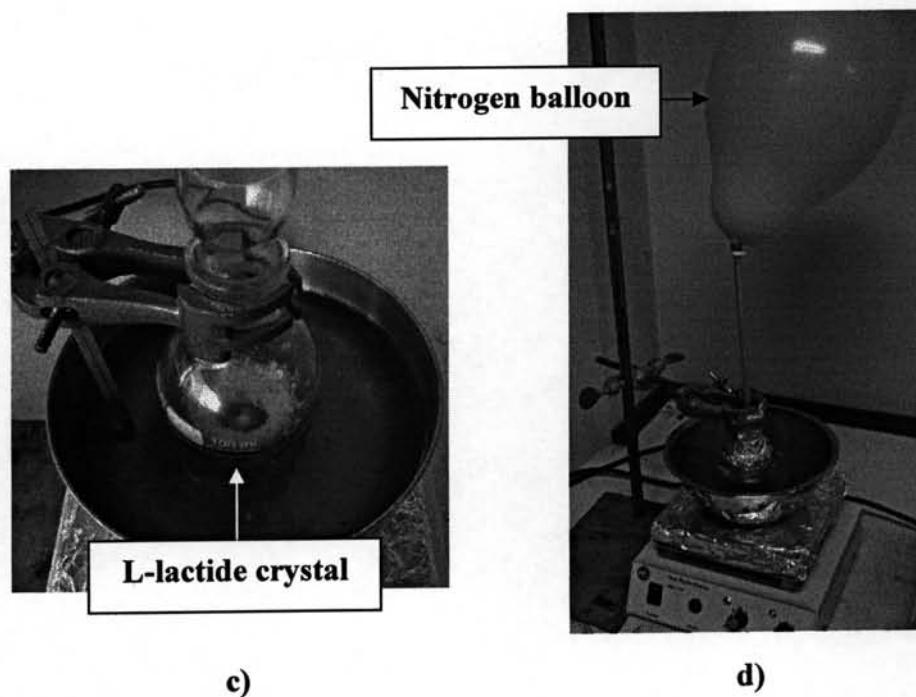


Figure 4.3 c) L-lactide (2.0 g) in round bottom flask and d) Experimental set up for PLLA synthesis under nitrogen atmosphere.

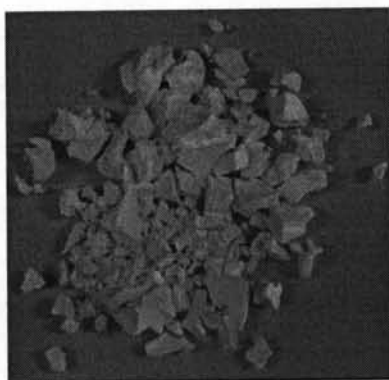


Figure 4.4 Poly(L-lactic acid) semicrystalline.

The purity of PLLA product was investigated by NMR technique. From ^1H NMR spectrum in Figure A-3, chemical shift at 5.16 ppm was assigned for $-\text{CHCH}_3$ group, and 1.57 ppm for CHCH_3 group. The spectrum of ^{13}C NMR in Figure A-4 was shown at 169 ppm for $-\text{COO}$ group, 69 ppm for $-\text{COH}$ group, and 16 ppm for CH_3 group.

4.2.1 Effect of initiator

4.2.1.1 Sn(Oct)₂

L-lactide and Sn(Oct)₂ (the weight ratio of catalyst to L-lactide is 0.3:100) was heated in bulk at 120°C and the reaction time was varied at 12, 24, and 48 hours.

Table 4.2 \overline{M}_w , \overline{M}_n , yield, and physical appearance of PLLA prepared in bulk solution at 120°C under N₂ atmosphere with weight ratio of Sn(Oct)₂ to L-lactide of 0.3:100.

	Reaction time (hours)	% yield	GPC			Physical Appearance
			\overline{M}_w	\overline{M}_n	PDI	
1	12	61.33±3.88	4947	4090	1.21	white
2	24	82.17±5.01	11040	8642	1.28	white
3	48	55.33±5.03	5714	4807	1.19	white

In Table 4.2, the molecular weight, yield and physical appearance of the crude products are shown. They are depending on reaction time. If the reaction time was too long the PLLA products were decomposed to L-lactic acid and oligomer which were soluble in excess methanol. For this reason, the long reaction time will give lower yield and molecular weight of PLLA than that of the short reaction time. The highest molecular weight and yield were obtained at 120°C, 24 hours. Crude product was yellow solid which dissolved in methylene chloride and precipitated with excess methanol. The white solid PLLA was centrifuged to separate it from light yellow solution. Then, white pure PLLA solid was dried in vacuum oven at 50°C for 1 day.

4.2.1.2 Creatine hydrate

Creatine hydrate is a recent non heavy metal catalyst used in PLLA synthesis. Due to its low toxicity, this catalyst is suitable for use in PLLA polymerization for medical and food applications [1].

The L-lactide and creatine hydrate (the weight ratio of catalyst to L-lactide is 0.3:100) was placed in 25 ml round bottom flask, and heated in silicone oil bath under nitrogen atmosphere. Reaction temperature was varied at 100, 120, 140, and 160°C and reaction time at 24, 48, and 96 hours.

4.2.2 Reaction temperature

The first parameter which was studied in this research was the effect of temperatures. Temperature range was also dependent on type of catalysts. Stannous(II) 2-ethylhexanoate was used to initiate polymerization at 120-150 °C. Creatine hydrate was used to initiate polymerization at 100-160 °C [32].

Table 4.3 \overline{M}_w , \overline{M}_n , yield, and physical appearance of PLLA prepared in bulk solution in 96 hours under N₂ atmosphere with weight ratio of creatine hydrate to L-lactide of 0.3:100.

	Temperature (°C)	% yield	GPC			Physical Appearance
			\overline{M}_w	\overline{M}_n	PDI	
1	100	37.50±2.18	5260	4539	1.16	white
2	120	56.50±3.61	5345	4729	1.13	white
3	140	45.00±0.50	7005	5786	1.21	white
4	160	DC*	DC*	DC*	DC*	viscous dark brown liquid

DC* = Decomposition of PLLA – NMR spectrum was shown signals of PLLA, monomer and impurities.

From Table 4.3, the highest yield can be produced at 120°C. However, high molecular weight PLLA could not be obtained at this condition. The suitable temperature for producing high molecular weight PLLA was 140°C. At 160°C PLLA was decomposed and changed to dark brown color.

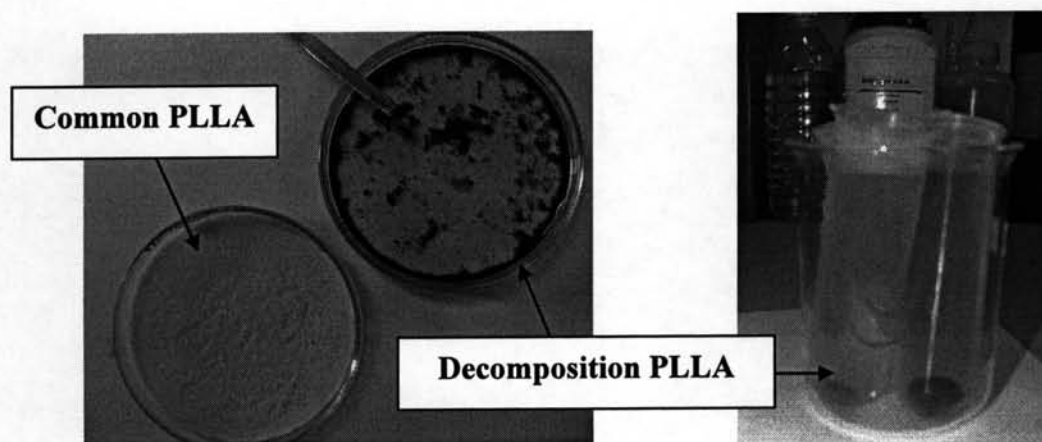


Figure 4.5 Comparison of between decomposed PLLA and crude PLLA.

High reaction temperature gave high yield and high molecular weight PLLA. However, very high reaction temperature could be decomposed PLLA.

4.2.3 Reaction time

Polymerization time is dependent on type of catalyst. High molecular weight PLLA can be obtained from long reaction time. However, if the reaction time was too long, the PLLA would decompose to L-lactic acid and oligomer. In order to study about condition details which gave the highest yield PLLA, the reaction temperature was fixed at 120°C and reaction time was varied from 24, 48, and 96 hours.

Table 4.4 \overline{M}_w , \overline{M}_n , yield, and physical appearance of PLLA prepared in bulk solution at 120°C under N₂ atmosphere with weight ratio of creatine hydrate to L-lactide of 0.3:100.

	Reaction time (hours)	% yield	GPC			Physical Appearance
			\overline{M}_w	\overline{M}_n	PDI	
1	24	37.10±1.85	5440	4669	1.17	white
2	48	42.17±2.75	6664	5604	1.19	white
3	96	56.50±3.61	5345	4729	1.13	white

In Table 4.4, at the condition of 96 hours, 120°C gave the highest yield of PLLA whereas, the highest molecular weight PLLA was produced at 48 hours, 120°C.

From the above report (Table 4.2-4.4), suitable condition for Sn(Oct)₂ was 120°C, 24 hours. The creatine hydrate produced the highest yield PLLA at 120°C, 96 hours and the highest molecular weight at 140°C, 96 hours. Under the same reaction temperature (120°C), Sn(Oct)₂ produce higher molecular weight and yield than creatine hydrate. However, creatine hydrate was non-heavy metal initiator which was suitable for food products.

4.3 Chain extension of PLLA

In this step the color of crude PLLA was changed to more yellow than before and too sticky. The crude product was dissolved in methylene chloride and precipitated with excess methanol. The white participant was dried in vacuum oven for 1 day.

4.3.1 Chain extender

In this research, two types of chain extenders (HMDI [18-20] and tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer) have been used. The effect of ratio of PLLA to chain extender on PLLA, molecular weight and PDI was observed.

Table 4.5 \overline{M}_w , \overline{M}_n and PDI of PLLA prepared in bulk solution at 140°C using two types of chain extender in excess ratio of PLLA to chain extender of 1:1.1.

Condition	Sample	Chain extender	GPC		
			\overline{M}_w	\overline{M}_n	PDI
PLLA	1	w/o	11040	8642	1.28
(Sn(Oct) ₂ , 120°C, 24 hr.)	2	HMDI ^a	13458	8555	1.57
	3	Tolylene ^b	22873	12095	1.89
PLLA (creatine hydrate, 120°C, 24 hr.)	4	w/o	5440	4669	1.17
	5	HMDI ^a	7182	5535	1.30
	6	Tolylene ^b	26666	13907	1.92
PLLA (creatine hydrate, 120°C, 48 hr.)	7	w/o	6664	5604	1.19
	8	HMDI ^a	8512	7432	1.15
	9	Tolylene ^b	21824	11138	1.96

w/o = without chain extender in reaction, a = 1,6-hexamethylene diisocyanate
b = tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer

From Table 4.5, the results indicated that chain extender which contained diisocyanate groups could be used to increase the molecular weight of PLLA. In addition, the novel chain extender, tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer, could produce higher molecular weight than the commonly used 1,6-hexamethylene diisocyanate.

4.3.2 Effect of ratio of PLLA to chain extender

The effect of ratio of PLLA to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer was studied at 1:0.5, 1:1.1, and 1:2.

Table 4.6 \overline{M}_w , \overline{M}_n and PDI of PLLA prepared in bulk solution at 140°C using different ratio of PLA to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer.

Condition	Sample	PLA : Tolylene	GPC		
			\overline{M}_w	\overline{M}_n	PDI
PLLA (Sn(Oct) ₂ , 120°C, 24hr.)	1	w/o tolylene	5611	4473	1.25
	2	1:0.5	19921	10989	1.81
	3	1:1.1	22511	8853	2.54
	4	1:2.0	25761	11497	2.24
PLLA (Sn(Oct) ₂ , 120°C, 24hr.)	5	w/o tolylene	8693	6313	1.38
	6	1:0.5	14682	9449	1.55
	7	1:1.1	25202	16622	1.52
	8	1:2.0	29480	18020	1.64
PLLA (Sn(Oct) ₂ , 120°C, 48hr.)	9	w/o tolylene	5714	4807	1.19
	10	1:0.5	18646	10816	1.72
	11	1:1.1	28789	16345	1.76
	12	1:2.0	29514	15853	1.86
PLLA (creatine hydrate, 120°C, 24 hr.)	13	w/o tolylene	5440	4669	1.17
	14	1:0.5	21681	8753	2.48
	15	1:1.1	26666	13907	1.92
	16	1:2.0	27188	12055	2.26
PLLA (creatine hydrate, 120°C, 48 hr.)	17	w/o tolylene	6664	5604	1.19
	18	1:0.5	21758	11100	1.96
	19	1:1.1	21824	11138	1.96
	20	1:2.0	21923	9905	2.21

w/o = without chain extender in reaction

Effect of ratio of PLLA to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer was investigated (Table 4.6). The high molecular weight PLLA was obtained by increasing the number of tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer. The other research [19-20] reported that the optimal ratio of PLLA to chain extender was at 1:1.1 because it was found that the complete reaction could be obtained in excess chain extender. However, tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer was over, the reaction mixture will be too sticky and physical properties of polymer obtained will be change.

From Table 4.6, \overline{M}_w of all of sample at the ratio of 1:0.5, 1:1.1 and 1:2 was slightly increased depending on the amount of tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer. The shape of GPC chromatogram indicates more details of \overline{M}_w , \overline{M}_n and PDI at different ratio of PLLA to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer.

According to GPC chromatogram shown in Figures 4.7-4.10, high molecular weight PLLA cannot pass through the porous structure of gel in column; therefore, it is eluted from column prior to low molecular weight PLLA. For this reason, shorter retention time indicates higher molecular weight of PLLA as the highest peak in the chromatogram shifts to the left side of the x-axis.

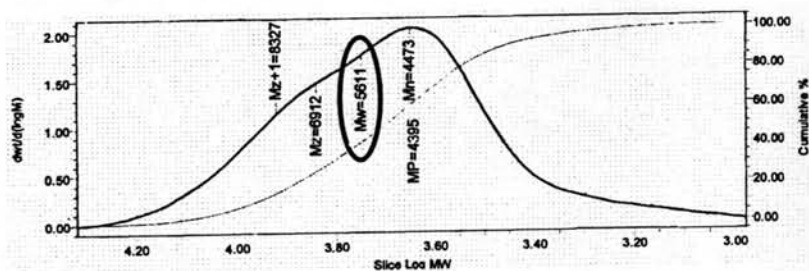


Figure 4.6 The chromatogram of sample 1: PLLA ($\text{Sn}(\text{Oct})_2$, 120°C , 24hr.) without tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer ($\overline{M}_w = 5611$).

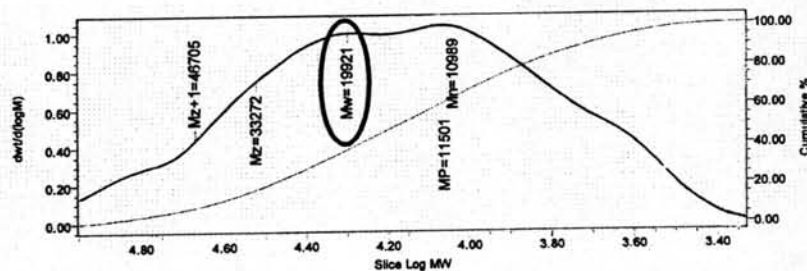


Figure 4.7 The chromatogram of sample 2: PLIA ($\text{Sn}(\text{Oct})_2$, 120°C , 24hr.) to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer is 1:0.5 ($\overline{M}_w = 19921$).

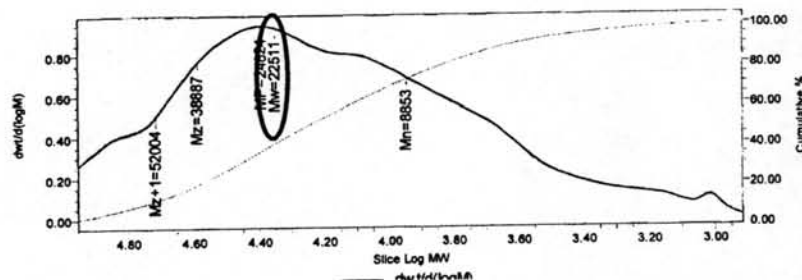


Figure 4.8 The chromatogram of sample 3: PLLA ($\text{Sn}(\text{Oct})_2$, 120°C , 24hr.) to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer is 1:1.1 ($\overline{M}_w = 22511$).

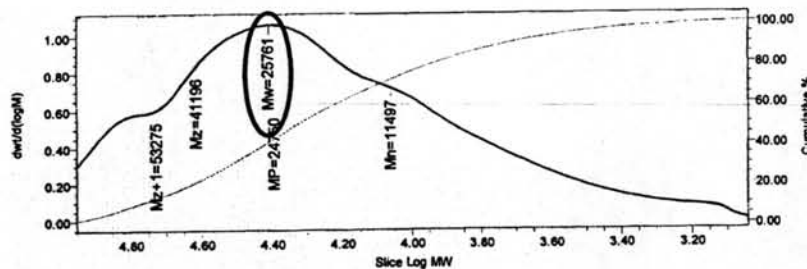


Figure 4.9 The chromatogram of sample 4: PLLA ($\text{Sn}(\text{Oct})_2$, 120°C , 24hr.) to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer is 1:2.0 ($\overline{M}_w = 25761$).

In order to investigate the peak in GPC chromatogram and \overline{M}_w and \overline{M}_n values in Table 4.6, the samples 5-20 were studied. This research compared four series of each PLLA low molecular weight reactant. The relationship of four series of GPC graph in sample 5-8, 9-12, 13-16, and 17-20 are shown the same in appendix B.

The results from GPC analysis indicate that the highest molecular weight of PLLA was obtained when using chain extender at the ratio of 1:2. However, the physical properties of PLLA might be deviated at the high ratio of chain extender to polymer. To determine the effect of chain extender on the physical properties of polymer, T_g was observed by DSC. When the temperature of the polymer is lower than T_g , the polymer becomes glass-like resulting in brittle polymer. At higher temperature than T_g , the polymer becomes rubber-like showing more elastic property.

Table 4.7 The glass transition temperature of PLLA in figures 4.10-4.13.

Figure	\overline{M}_w	PLLA:Tolylene	T_g (°C)
4.10	5714	w/o Tolylene	28.6
4.11	18646	1:0.5	48.6
4.12	28789	1:1.1	45.1
4.13	29514	1:2.0	Could not be detected

w/o = without chain extender in reaction

The results in Figures 4.10-4.13 indicate that the more the chain extenders, the higher T_g was obtained. Besides, T_g could not be detected when using excess chain extender. This indicates that the physical properties of polymer have been changed.

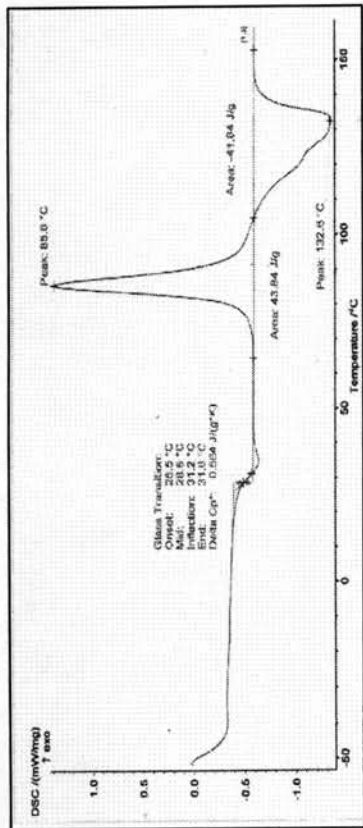


Figure 4.10 The DSC chromatogram of PLLA sample 9.

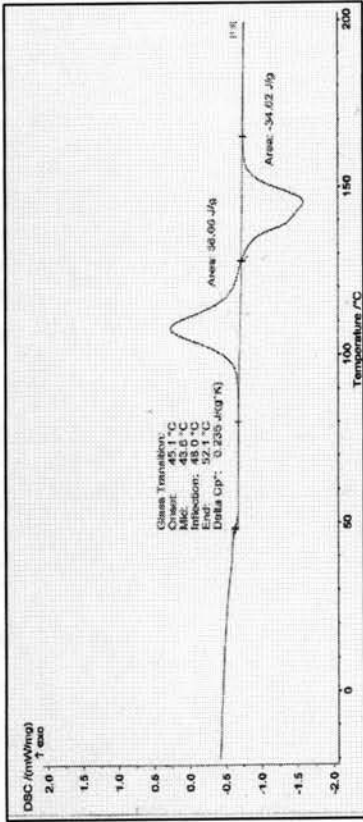


Figure 4.11 The DSC chromatogram of PLLA sample 10.

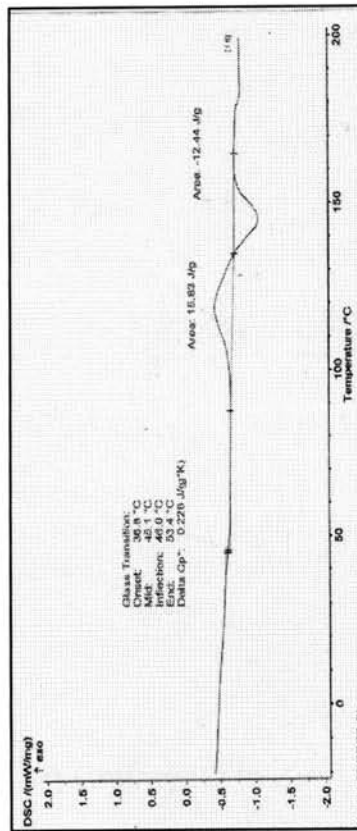


Figure 4.12 The DSC chromatogram of PLLA sample 11.

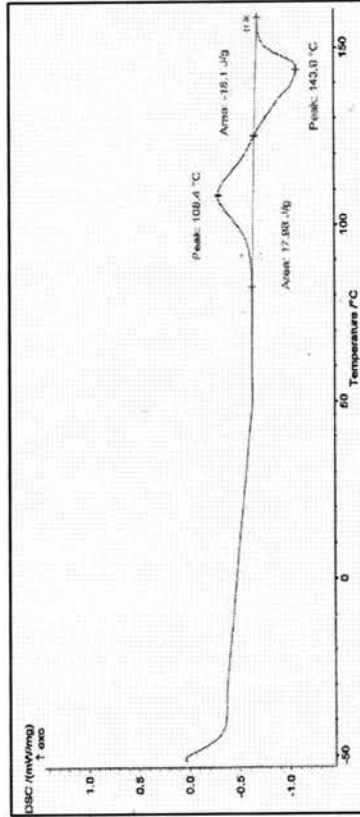


Figure 4.13 The DSC chromatogram of PLLA sample 12.

This result could be described that, high molecular weight PLLA which using tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer as the chain extender was contained $-NH$ group in PLLA chain. This group was formed hydrogen bond with carbonyl group of the other PLLA chain and difficult to move more than PLLA without chain extender. In this reason, the T_g was increased from $28.6^{\circ}C$ to $48.6^{\circ}C$ and $45.1^{\circ}C$ respectively.

On the other hand, the nature of tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer was difficultly detected T_g because it was similarly an elastomer. The excess tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:2 was difficultly detected T_g too. The DSC was used to analyze T_g two times and both of them could not be detected T_g . Surely that, the physical property of PLLA was completely changed to the most likely tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer.