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SYNTHESIS AND CHAIN EXTENSION OF BRANCHED POLY(L-LACTIDE)

Mr. Natthaphon Suksamran



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

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การสังเคราะห์พอลิแอลแล็กไทด์แบบโซ่กิ่งให้มีน้ำหนักโมเลกุลสูงใช้ 2 ขั้นตอน ขั้นตอนแรกสังเคราะห์พอลิแอลแล็กไทด์แบบโซ่ตรงและแบบโซ่กิ่งจากวิธีพอลิเมอไรเซชันแบบเปิดวง น้ำหนักโมเลกุลที่ได้อยู่ในช่วง 10,000 – 38,000 กรัม/โมล ขั้นตอนที่สองเป็นการขยายสายโซ่ของพอลิแอลแล็กไทด์แบบโซ่กิ่ง โดยการเชื่อมพอลิแอลแล็กไทด์แบบโซ่ตรงเข้าด้วยกันผ่านหมู่ไฮดรอกซิลที่ปลายของสายโซ่โดยใช้เฮกซะเมทิลีน ไดไอโซไซยานาท (HDI) เป็นตัวเชื่อมต่อ ทำปฏิกิริยาในสารละลายโดยใช้ไซลีนเป็นตัวทำละลายที่อุณหภูมิ 110 องศาเซลเซียส เริ่มจากใช้พอลิแอลแล็กไทด์เริ่มต้นที่มีน้ำหนักโมเลกุล 20,000 กรัมต่อโมล ได้พอลิแอลแล็กไทด์แบบโซ่กิ่ง 3 แขนที่มีน้ำหนักโมเลกุลสูงถึง 55,000 กรัม/โมล เมื่อใช้อัตราส่วนโดยโมลของพอลิแอลแล็กไทด์แบบโซ่กิ่ง/แบบโซ่ตรง/ตัวเชื่อมต่อเป็น 1/3/6 ใช้เวลาในการทำปฏิกิริยา 3 ชั่วโมง การใช้ HDI ที่มากเกินไปนำมาสู่การเกิดเจลที่ไม่ละลายในตัวทำละลาย พอลิแอลแล็กไทด์แบบโซ่กิ่งที่มีน้ำหนักโมเลกุลสูงเกิดผลึกได้ดีกว่าและมีอุณหภูมิการสลายตัวทางความร้อนสูงกว่าพอลิเมอริ์เริ่มต้น การเติมพอลิแอลแล็กไทด์แบบโซ่กิ่งไปในพอลิแอลแล็กไทด์แบบโซ่ตรงนั้นสามารถปรับปรุงความแข็งแรงในการไหล (melt strength) ได้อีกด้วย

จุฬาลงกรณ์มหาวิทยาลัย  
 CHULALONGKORN UNIVERSITY

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High molecular weight branched poly(L-lactide) (PLLA) was prepared by a two-step method. In the first step, linear and branched PLLAs were synthesized via ring opening polymerization (ROP). The obtained molecular weights were in the range of 10,000 – 38,000 g/mol. In the second step, the branched PLLA chain was extended by joining linear PLLA chains together via the terminal hydroxyl groups using hexamethylene diisocyanate (HDI) as chain extender. All reactions were performed in solution using xylene as the solvent, at 110 °C. Starting from PLLA prepolymer with molecular weight of 20,000 g/mole, the final extended 3-arm branched PLLA with molecular weight as high as 55,000 g/mol was obtained when the mole ratio of branched PLLA/linear PLLA/chain extender as 1/3/6 and the reaction time of 3 hr. Using excess HDI, however, yielded polymer gel that was not dissolved in the solvent. High molecular weight branched PLLA formed higher crystallinity and withstood higher thermal decomposition temperature than the prepolymers. Adding branched PLLA into linear PLLA could also improve its melt strength.

Field of Study: Petrochemistry and  
Polymer Science

Student's Signature .....  
Advisor's Signature .....

Academic Year: 2014

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## LIST OF ABBREVIATIONS

BA	: Benzyl alcohol
CDI	: 1,1'-Carbonyl diimidazole
CDI1	: PLLA reacted with CDI at the 1 <sup>st</sup> condition
DSC	: Differential scanning calorimetry
FT-IR	: Fourier transform infrared
GL	: Glycerol
GPC	: Gel permeation chromatography
HDI	: Hexamethylene diisocyanate
HDI1	: PLLA reacted with HDI at the 1 <sup>st</sup> condition
HPLC	: High performance liquid chromatography
$\Delta H_{cc}$	: Fusion enthalpy
$\bar{M}_n$	: Number-average molecular weight
$\bar{M}_w$	: Weight-average molecular weight
NMR	: Nuclear magnetic resonance spectroscopy
PLLA	: Poly(L-lactide) or poly(lactic acid)
PLLA-pre	: PLLA before chain extension
ROP	: Ring-opening polymerization
Sn(Oct) <sub>2</sub>	: Tin(II) 2-ethylhexanoate
THF	: Tetrahydrofuran
T <sub>cc</sub>	: Cold crystallization temperature during cooling
T <sub>m</sub>	: Melting temperature
TGA	: Thermal gravimetric analysis
X <sub>cc</sub>	: Crystallinity at T <sub>cc</sub>
X <sub>cc</sub>	: Crystalline at T <sub>m</sub>

# CHAPTER 1

## INTRODUCTION

### 1.1 Statement of Problem

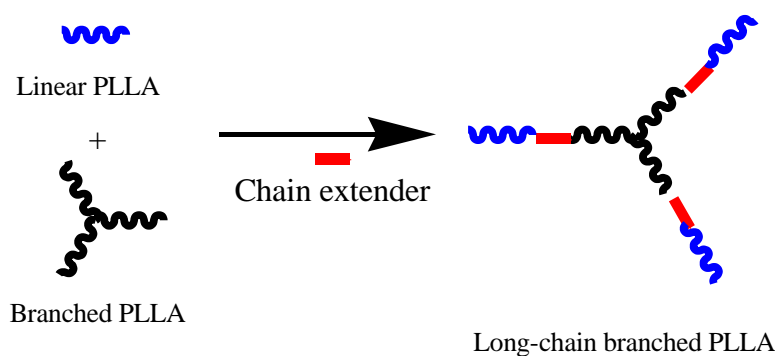
Recently, biodegradable plastics have received much more interest due to a dramatic increase in environmental concerns. Among a variety of biodegradable plastics, poly(lactic acid) or poly(L-lactide) (PLLA) is one of the best known commercially-available aliphatic polyesters. PLLA finds its extensive using as agricultural, medical devices, fisheries, food packaging, civil engineer, toiletry, and outdoor sports [1].

PLLA can be synthesized by two methods: polycondensation and ring-opening polymerization (ROP) [2-4]. In polycondensation method, lactic acid is used as monomer in the polycondensation process in which water is a by-product. Generally PLLA from this method has low molecular weight because removal of the water by-product from viscous polymer product is rather difficult. In the ROP method, the monomer is lactide, a six-membered cyclic di-ester, obtained from two molecules of lactic acid. The ROP proceeds with the help of catalyst and no by-product forms. The molecular weight PLLA from this method is generally higher than the one from polycondensation [1, 5].

However, linear PLLA has very low melt strength, which limits its processing, such as extrusion, film blowing, and foaming. One method that can overcome this problem is by adding long-chain branched polymer [6-8]. An increase in entanglements between the long-chain branches and nearby polymer chains in the melt and concentrated solutions can take place [9]. Nevertheless making a long-chain branched structure always faces one obstacle; steric effect, that could somewhat reduce the number of branching and/or the length of each branch.

The purpose of this research was to synthesize long-chain branched PLLA. All polymerizations, linear and branched PLLA, were carried out by the ROP method from poly(L-lactide). Then the linear PLLA was covalently linked to the branched

PLLA by the use of chain extenders. The two types of chain extender used in this study were hexamethylene diisocyanate (HDI) and 1,1'-carbonyl diimidazole (CDI).



**Scheme 1.1** The linear and branched PLLAs linked to the long-chain branched PLLA by the use of chain extender.

## 1.2 Objectives

The aim of this study was to synthesize long-chain branched PLLA by connecting linear and branched PLLA prepolymers together using chain extender molecules. Two chain extenders tested were hexamethylene diisocyanate (HDI) and 1,1'-carbonyl diimidazole (CDI).

## 1.3 Scope of Investigation

1. Synthesis of linear and branched PLLA prepolymer by the ROP with lactide as monomer.
2. Connecting the linear and branched PLLA by using a chain extender. Two chain extenders studied here were HDI and CDI.
3. Preparation of blended polymers consisting of linear and long-chain branched PLLA with internal mixer.
4. Characterization of the long-chain branched PLLA compared with the blend samples by nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ), Fourier transform-infrared spectroscopy (FT-IR), gel permeation chromatography

(GPC), differential scanning calorimeter (DSC), thermal gravimetric analysis (TGA), and capillary rheometer.

5. Result discussion and summary.



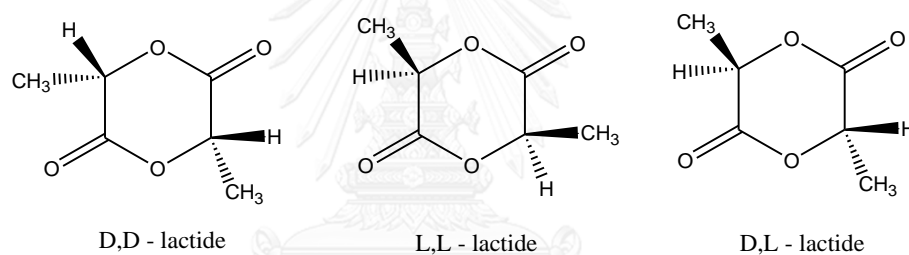


## CHAPTER 2

### THEORY AND LITERATURE REVIEW

#### 2.1 Lactide

Lactide is monomer of polylactide (PLLA), which can be produced from decomposition of PLA oligomer under reduced pressure. Its molecular formula is  $C_6H_8O_4$ , molar mass 144.13 g/mol, and melting temperature 98.7 °C. Molecule is a six membered cyclic di-ester, thus the form of lactide contains three enantiomers, such as DD-lactide, LL-lactide, and DL-lactide (meso-lactide) (Scheme 2.1), depend on its the form of lactic acid [10, 11].



**Scheme 2.1** Three isomers of lactide.

#### 2.2 Poly(lactide)

Poly(lactide) or poly(lactic acid) (PLLA) is semi-crystalline and compostable polyester, which is polymerized from lactic acid as monomer. Lactic acid is produced from renewable resource, such as corn and sugar cane. Hence, PLLA is also biopolymer (also called renewable polymer). Due to lactic acids have 2 optical isomers, L-lactic acid and D-lactic acid, thus PLLA has three forms: poly(L-lactide), poly(D-lactide), and poly(DL-lactide). Each form of PLLA effects to its properties [10]. The thermal properties of PLA, has a melting point about 170-183 °C and a glass-transition temperature about 55-65 °C [1, 2].

Although PLLA has many advantages, such as produced from renewable resource, high melting temperature, and compostable polymer. PLLA has also

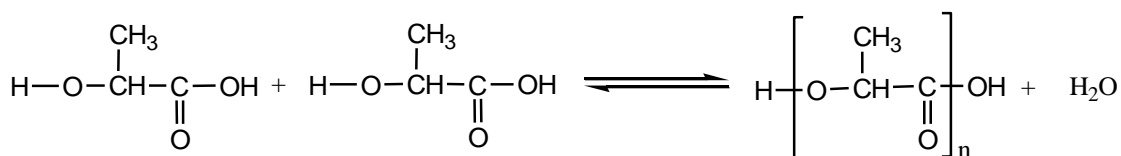
disadvantages, such as more expensive than other polymer, high hydrophilic effects to increasing hydrolysis or transesterification, brittle, and difficult for processing [5, 12].

PLA is synthesized via two main methods: polycondensation and ring-opening polymerization (ROP). The molecular weight of the first method is lower than the second method [5].

### 2.2.1 Polycondensation

This method is PLLA polymerization from lactic acid monomer. The hydroxyl group of lactic acid reacts with alongside carboxyl group of the another one via esterification reaction as shown in Scheme 2.2. The by-product of this reaction is water, which is complicated for removing from the highly viscous product. This water can react with ester repeating unit of the product via transesterification reaction. Therefore PLLA product is degraded, low molecular weight of PLLA is obtained [10, 12].

Although, this method obtains low molecular weight PLLA. Chain extension or coupling agent has used for increasing the molecular weight of PLLA. Chain extender is bi-functional group, such as hexamethylene diisocyanate [13-16], 1,4-butane diisocyanate [17], 1,1'-carbonyldiimidazole [18], 1,4-butanediol [13, 17, 19, 20], and so on. It will be explained in the next topic.



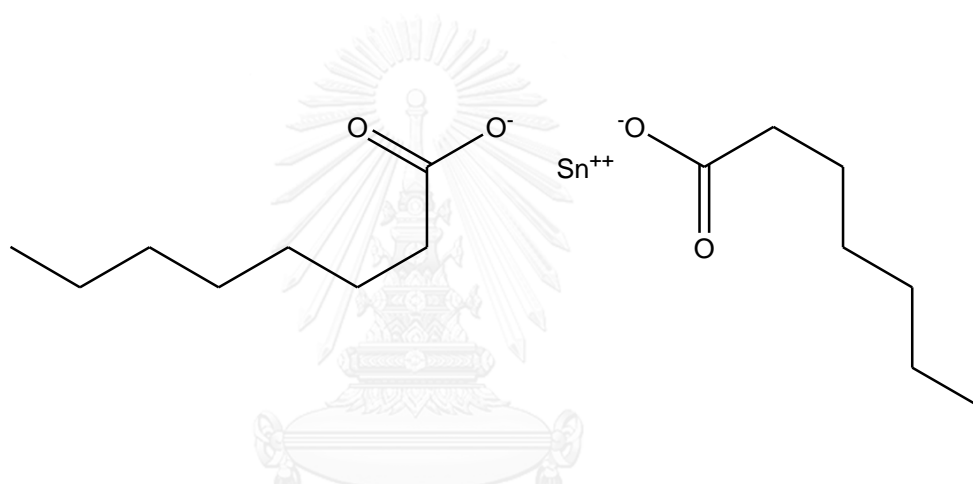
**Scheme 2.2** Polycondensation of lactic acid to be PLLA.

### 2.2.2 Ring-Opening Polymerization

The ring-opening polymerization (ROP) of PLLA is an polymerization of the chain end of polymer acts with lactide monomer to growth to high molecular weight.

This method does not have by-product. The molecular weight of product is rather high, in the range 20,000-600,000 g/mol, depend on the type catalyst [21].

Tin(II) bis-2-ethylhexanoic acid or stannous octoate  $[\text{Sn}(\text{Oct})_2]$  (Scheme 2.3) is one of catalyst, which is high activity, solubility in several solvents and dissolved in lactide monomer, easy for storage, and stable for heating (up to 180 °C). In addition, the FDA (Food and drug Administration) approved for toxic [10, 21]. However, the addition of hydroxyl group effects to polymerization rate [22]. The most favorite hydroxyl molecule is alcohol, such as benzyl alcohol. Because its incorporation as benzyl ester end group is easily detectable by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [23].



**Scheme 2.3** Tin (II) 2-ethylhexanoate or stannous octoate  $[\text{Sn}(\text{Oct})_2]$ .

### 2.2.3 Branched PLLA

Branched PLLA is defined to polymer contains chain arms more than two (linear PLLA). For the same molecular weight, the polymer chain arms of branch are shorter than linear.

Increasing branching effects to the PLLA properties as shown in table 2.1 [13, 24, 25]. Crystallinity decreases with increasing branching, having packing of chain is difficult. The melting temperature of branched is lower than linear PLLA due to increase the short chain of branching, leading to free chain ends, which retards the forming of crystal. So having branching increases the amorphous part of PLLA. In addition, increasing number of chain end or hydroxyl group effect to lead degradation of PLLA with transesterification reaction. Furthermore, branched PLLA

can increase melt strength with the forming of chain entanglement, which decreases the problem of PLLA processing [13].

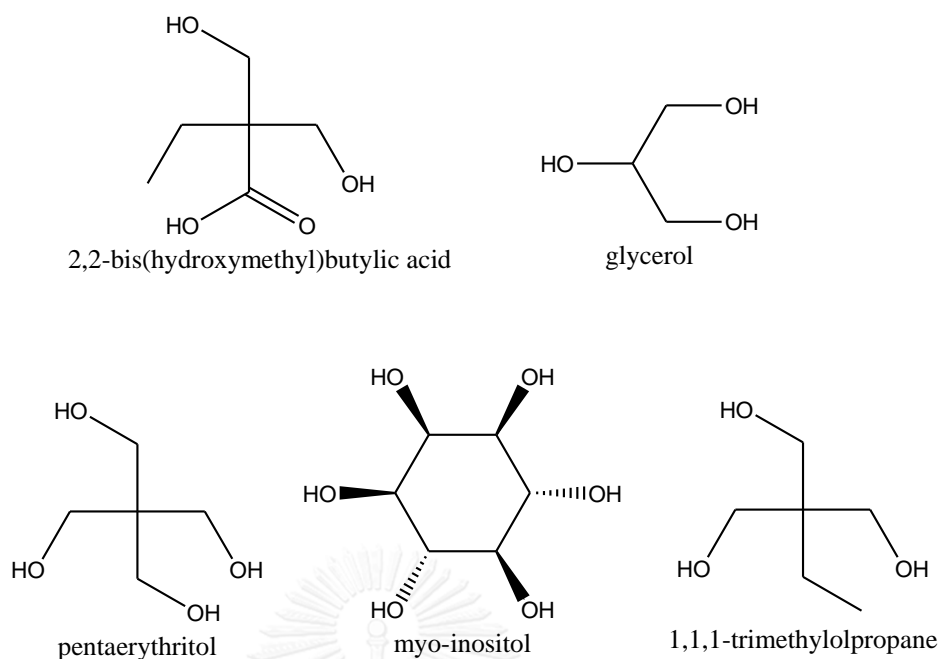
**Table 2.1** Comparison of properties for linear and linear/long-chain branch blending.

Linear	Linear/long-chain branch blending
Poor melt strength	High melt strength
Poor impact strength	High impact strength
Low elongation at break	High elongation at break
Low heat deflection temperature	More significant shear thinning
	Fast crystallization rate
	Improved foaming ability

The methodologies of branched synthesis have many routes as [24]:

1. Using a multifunctional as comonomer or initiator

Multifunctional comonomers like glycerol [26], pentaerythritol[19, 27, 28], polyglycerine [19], 1,1,1-trimethylolpropane [13, 20], myo-inositol [27], 2,2-bis(hydroxymethyl) butyric acid [29], polyglycidol [30], and polyamidoamine [31] were prepared multi chain polymer, which number of chain accords with the number of functional group.

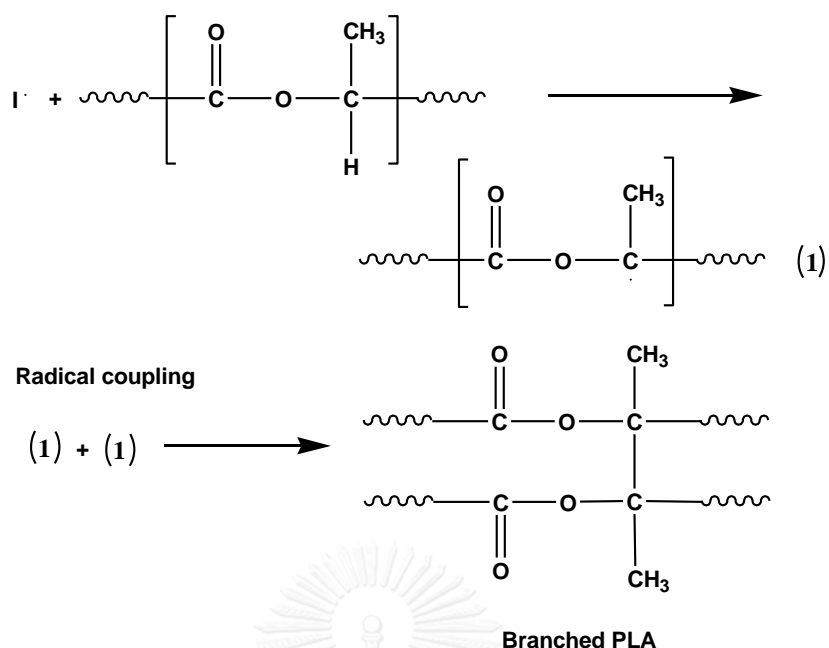


**Scheme 2.4** Multifunctional comonomer for the synthesis of branched PLLA.

In 1995, Arvanitoyannis et al [26], prepared star-shaped polylactide with glycerol using tetraphenyl tin or  $\text{Sn}(\text{Oct})_2$  as catalyst and lactide as monomer. The molar ratios of monomer to glycerol was been various in the length 3/1 to 100/1. The  $\bar{M}_n$  of branched PLLA was in length of 1,400-14,000 g/mol. Efficiency of  $\text{Sn}(\text{Oct})_2$  was better than tetraphenyl tin. The degradation temperature of low  $\bar{M}_n$  was higher than the one of high  $\bar{M}_n$ . It can be explained that, the low molecular weight PLLA had much more hydroxyl group at the chain end, the hydroxyl group led to fast degradation of PLLA by transesterification reaction.

## 2. Using free radical crosslinking with peroxides after polymerization

This method of increasing branching is reaction of PLLA with peroxide, PLLA has an active hydrogen which can be abstracted using peroxide which results in free radicals along the backbone of the PLLA. However, this method is usually difficult to control reaction. The obtained PLLA was crosslinking polymer, which can not use in the processing to product [24, 32].



Scheme 2.5 Branched PLLA from using peroxid.

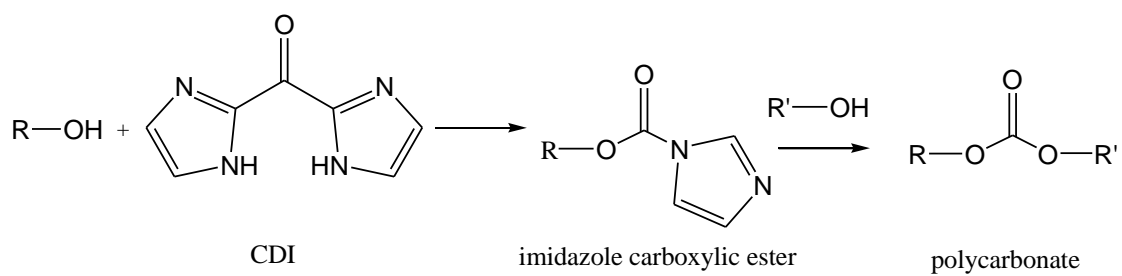
### 2.3 Chain extension of Polymer

The role of chain extender was to join two polymer chain ends together. In the PLLA chain, the hydroxyl end-groups of two prepolymers can react with a bi-functional molecular weight compound, called chain extender or coupling agent. Examples of chain extender for PLLA are hexamethylene diisocyanate (HDI) [13-16], 1,4-butane diisocyanate [17], 1,1'-carbonyldiimidazole [18], 1,4-butanediol [13, 17, 19, 20], and so on.

Isocyanate is high active functional group for PLLA. It has used in production of urethane foam [14, 15]. In 1995, Woo et al [14] reported synthesis of high molecular weight PLLA using HDI as chain extender. The first step, PLLA prepolymer was synthesized by direct polycondensation method by using lactic acid as monomer. The second step, the HDI was added into prepolymer for chain extension at 160 °C for 10 min. The obtained maximum  $\bar{M}_n$  was 33,000 g/mol. It found that the  $\bar{M}_n$  increased when CDI was increased.

In the 1,1'-carbonyl diimidazole (CDI) system, it is a coupling agent that can be used to form carbonates, esters, ureas, urethanes, and amides [33]. In 1999 and 2000, Rannard et al [34, 35] studied the synthesis of polycarbonate via reaction of

alcohol and CDI to obtain imidazole carboxylic ester as intermediate. After that, the intermediate was reacted with another alcohol for forming polycarbonate product as shown in scheme 2.6.



**Scheme 2.6** The synthesis of polycarbonate from CDI and alcohol.



## CHAPTER 3

### EXPERIMENTAL

#### 3.1 Materials

Lactide was purchased from Department of Chemistry, Faculty of Science, Chiang Mai University. Tin (II) ethylhexanoate [Sn(Oct)<sub>2</sub>], benzyl alcohol (BA), glycerol (GL), hexamethylene diisocyanate (HDI), and 1,1'-carbonyl diimidazole (CDI) were purchased from Sigma-Aldrich (USA). Ethyl acetate (EtOac), methanol (MeOH), chloroform (CH<sub>2</sub>Cl<sub>2</sub>), toluene (assay 98% min), xylene (assay 98% min), and tetrahydrofuran (THF) (HPLC grade) were purchased from RCI Labscan Limited (Thailand). PLLA pellet, grade 3251D was purchased from Nature Work (USA).

#### 3.2 Equipments

##### 3.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

PLLA was dissolved in deuterated chloroform (CDCl<sub>3</sub>). A Bruker Ascend 400 nuclear magnetic resonance spectrometer (Germany) was used to record <sup>1</sup>H-NMR spectra, operating at 400 MHz in room temperature. The peak positions were reported with tetramethylsilane (TMS) or the residual protonated solvent signal as a reference.

##### 3.2.2 Fourier Transform – Infrared Spectroscopy (FT-IR)

PLLA structure was characterized by a Bruker Vertex 70V Fourier transform infrared spectrometer.

##### 3.2.3 Gel Permeation Chromatography (GPC)

The molecular weight and molecular weight distribution of PLLA were measured by a Agilent Technology 1260 Infinity gel permeation chromatograph using



tetrahydrofuran (THF) (HPLC grade) as an eluent. Polystyrene standards ( $M_w$  715-2,422,000 Da) used for a calibration curve. The conditions were followed to:

Eluent:	Tetrahydrofuran (HPLC grade; Degassed)
Flow rate:	1.0 ml/min
Detector:	Refractive index (G1362A)
Injection volume:	100 $\mu$ l
Column:	PLgel 5 $\mu$ m 10E4A
Column particle Size:	5 $\mu$ m
Column Temperature:	35 $^{\circ}$ C

PLAs were dissolved in tetrahydrofuran (THF) (2mg/ml) for overnight and then filtered using nylon 66 membrane (pore size 0.45  $\mu$ m) before injection.

### 3.2.4 Differential Scanning Calorimetry (DSC)

DSC was scanned by using a Mettler Toledo DSC1 differential scanning calorimeter under nitrogen  $N_2$  atmosphere at flow rate 50 ml/min. The heat program was

- (i) Heating from 0  $^{\circ}$ C to 200  $^{\circ}$ C at the heating rate of 10  $^{\circ}$ C/min.
- (ii) Holding at 200  $^{\circ}$ C for 5 min
- (iii) Cooling from 200  $^{\circ}$ C to 0  $^{\circ}$ C at the cooling rate of 10  $^{\circ}$ C/min.
- (iv) Heating from 0  $^{\circ}$ C to 200  $^{\circ}$ C at the heating rate of 10  $^{\circ}$ C/min.

The DSC thermograms of cooling and second heating were recorded. In cooling step,  $T_{cc}$ (cold crystallization temperature during cooling) was evaluated. Second heating step,  $T_m$  (melting temperature) were evaluated. For crystallinity,  $X_{cc}$ (crystallinity at  $T_{cc}$ ) and  $X_m$ (crystallinity at  $T_m$ ) were calculated as follows.

$$X_{cc}(\%) = \frac{\Delta H_{cc}}{\Delta H_{m0}} \times 100$$

$$X_m(\%) = \frac{\Delta H_m}{\Delta H_{m0}} \times 100$$

where  $\Delta H_{cc}$ ,  $\Delta H_m$ , and  $\Delta H_{m0}$  were cold crystallization enthalpy at  $T_{cc}$ , fusion enthalpy, and fusion enthalpy of 100% crystalline (93.6 J/g), respectively.

### 3.2.5 Thermal Gravimetric Analysis (TGA)

The thermal decomposition temperature of PLLA was determined by a Mettler Toledo TGA/DSC1 thermal gravimetric analyzer using a heat program of 25 °C to 600 °C at heating rate 10°C/min under nitrogen atmosphere.

### 3.2.6 Internal Mixer

PLLA pellet and synthesized PLLA (50g) were mixed and took place in a Brabender 350E internal mixer with banbury blades type at 190 °C, time 10 minutes, and rotational speed 40 rpm. During testing, the corresponding torque and temperature curve was recorded.

### 3.2.7 Capillary Rheometer

PLLA, which was blended in internal mixer, was ground to be PLLA pellet before testing. The PLLA pellet (25 g) was added to the barrel of a Ceast Rheologic 2500 capillary rheometer with 10 mm die size and 1 mm diameter. The conditions were followed:

temperature	:	190 °C
piston position	:	150 mm
piston speed	:	1 mm/s
pre-heat time	:	3 minutes
pulley's starting velocity	:	50 mm/s
pulley's acceleration	:	0.5 mm/s

PLA extrudate was pulled by pulley until it was torn. During testing, the corresponding force and speed of pulley curve was recorded. The final force before tearing was reported as melt strength.

### 3.3 Methods

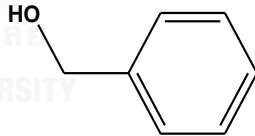
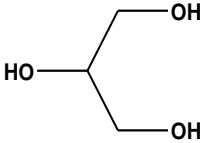
#### 3.3.1 Recrystallization of L-lactide

L-lactide (150 g) was added to a one-neck round bottom flask. Ethyl acetate (200 ml) as solvent was added into the flask, and then heated with heater mantle at 60°C until L-lactide was dissolved to homogeneous clear solution. Further, the flask was kept at room temperature for 24 hr. Finally, the crystals were filtered with vacuum oven at 30 °C for 24 hr. The dried crystals were confirmed the purity by the DSC machine.

#### 3.3.2 Synthesis of prepolymers

The prepolymer of this work had two architectures, such as linear and branched PLLAs, which used BA and GL as initiators for linear and branched PLLA, respectively. Table 3.1 shows the chemical structures of the initiators for this work.

**Table 3.1** Chemical structures of initiator for linear and branched PLLA prepolymers.

Initiator	Chemical structure
Benzyl alcohol (BA)	
Glycerol (GL)	

Synthesis of linear PLLA prepolymers followed the procedure reported by Arvanitoyannis in 1995 but with some modifications. The reaction temperature was raised to 140 °C instead of 130 °C in order to shorten the time and to prevent coagulation of rigid product.

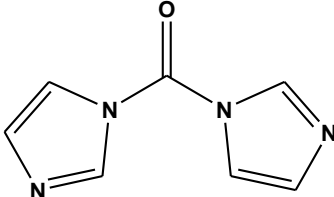
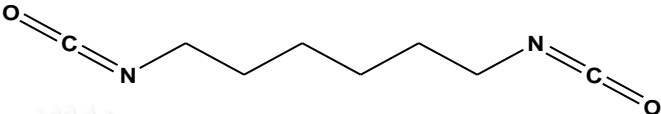
The Mbraun Labstar glove box was used for the preparation of reactor under  $N_2$  atmosphere to avoid moisture and oxygen gas, which damaged the activation of  $Sn(Oct)_2$  catalyst. For the synthesis of linear PLLA prepolymer, inside the glove box, a 500 ml 1-neck round bottom flask was charged with 20 g (0.14 mol) of L-lactide and various amounts of BA (BA/LLA = 1/80-1/250 mol/mol).  $Sn(Oct)_2$ /toluene stock solution (1 M) as 0.05 % mol/mol of L-lactide was then added. The reactor was sealed with silicone septum. Further, the reactor was taken out from the glove box and immersed into silicone oil bath at  $140^\circ C$  and with stirring for 24 hr under vacuum. The reaction was carried out until the viscosity was high enough and the magnetic bar was difficult to move. The vacuum pump was turned off and the white crude product was dissolved in chloroform before reprecipitating in 10-fold excess of cold methanol, and dried in vacuum oven at  $60^\circ C$  for 24 hr. The product was weighed and the yield was calculated.

The synthesis of branched prepolymer followed the same method with BA replaced by GL.

### **3.3.3 Chain extension of branched prepolymer with CDI and HDI as chain extenders**

Branched prepolymer was increased chain length with linear prepolymer in presence of chain extender as coupling agent. Two types of chain extender, CDI and HDI, were selected to study the efficiency in this work. Table 3.2 shows the chemical structures of two chain extenders for this work.

**Table 3.2** Chemical structures of chain extender.

Initiator	Chemical structure
1,1'-carbonyl diimidazole (CDI)	
Hexamethylene diisocyanate (HDI)	

The method of the chain extension followed the procedure of Noibuddee, which reported in 2010 [18]. Inside the glove box, a 50 ml 1-neck round bottom flask was charged with about 1g of prepolymers, which various mole ratios of branched to linear PLLA. Xylene (5 ml) as solvent was taken into the flask, and then was added the chain extender. The reactor was sealed with silicone septum and taken out from the glove box, and immersed in a silicone oil bath placed on a magnetic stirrer at fixed temperature at 110 °C to avoid evaporation of xylene solvent. The reaction time, molecular weight of prepolymer, and mole ratio of reaction were studied as listed in Table 3.3. The reaction was carried out until the viscosity was high enough and the magnetic bar was difficult to move. The vacuum pump was turned off and the white crude product was dissolved in chloroform before reprecipitating in 10-fold excess of cold methanol, and dried in vacuum oven at 60 °C for 24 hr. The product was weighed and the yield was calculated.

**Table 3.3** Variation of mole ratio of prepolymer : chain extender and reaction time.

Sample code	$\bar{M}_n$ of linear PLLA (g/mol)	$\bar{M}_n$ of branched PLLA (g/mol)	Molar ratio of branch/linear/chain extender	Reaction time (hr.)
PLLA-pre	10,410	11,473	1/3/0	3
HDI1	10,410	11,473	1/3/3	3
HDI2	10,410	11,473	1/3/6	3
HDI3	10,410	13,901	1/3/9	3
HDI4	11,014	10,410	1/3/12	3
HDI5	11,014	10,410	1/3/15	3
HDI6	11,014	12,374	1/3/6	0.5
HDI7	11,014	12,734	1/3/6	5
HDI8	11,014	12,734	1/3/6	10
HDI9	13,066	12,734	1/3/6	20
HDI10	20,793	12,866	1/3/6	3
HDI11	29,834	12,866	1/3/6	3
HDI12	34,890	12,866	1/3/6	3
HDI13	20,793	13,901	1/3/9	3
HDI14	29,834	13,901	1/3/9	3
HDI15	34,890	12,472	1/3/9	3

### 3.3.4 Determination of gel content

The 10 mg of PLLA was dissolved in chloroform (10 ml) for 24 hr. The solution was filtered with weighed Whatman grade No. 1 filter paper, which was dried in vacuum hot air oven. After that, the paper was washed with 20 ml of pure chloroform. The paper was dried in vacuum hot oven at 60 °C and was reweighed again. The percent of gel content was calculated by

$$\text{gel content (\%)} = \frac{\text{weight of paper after filtration}}{\text{weight of paper before filtration}} \times 100$$

The values reported in the results section were averaged from three sets of experiments.



## CHAPTER 4

### RESULTS AND DISCUSSION

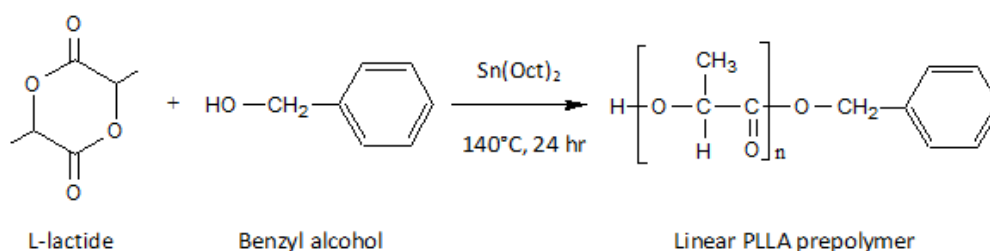
This chapter includes three parts. The first part referred to the syntheses and characterizations of linear and branched PLLA prepolymers. The second part referred to the chain extension of the prepolymers, which covered the types of chain extenders and the conditions of syntheses. The final part referred to the application of products, branched PLLA.

#### 4.1 Syntheses of linear and branched PLLA prepolymers by ring-opening polymerization

PLLA prepolymers were synthesized by the ROP method, which adapted from the procedure reported by Arvanitoyannis et al [26].

##### 4.1.1 Synthesis of linear PLLA prepolymer

Linear PLLA prepolymer was synthesized by ROP of L-lactide as monomer with benzyl alcohol as initiator as are shown in Scheme 4.1.

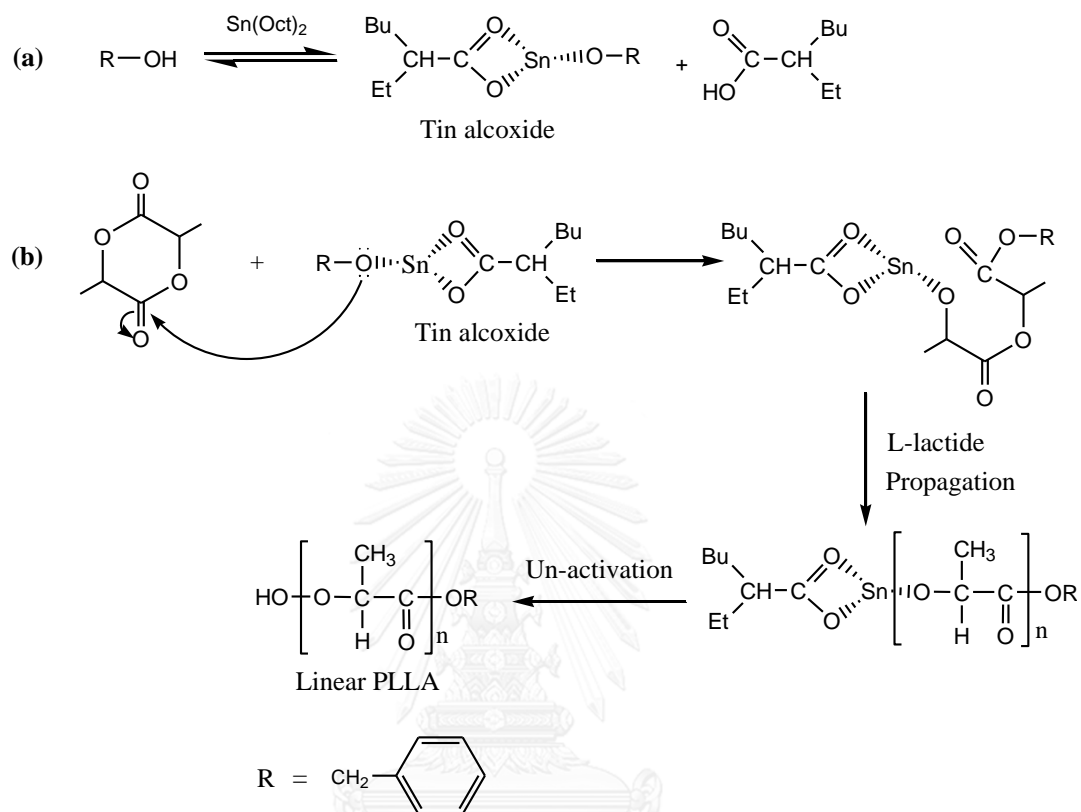


**Scheme 4.1** Synthesis of linear PLLA prepolymer from L-lactide.

The coordination-insertion mechanism of linear PLLA prepolymer synthesis in the presence of  $\text{Sn}(\text{Oct})_2$  is shown in Scheme 4.2. The first step (a), the hydroxyl group of BA exchanged with octoate ligand to become tin alkoxide. The second step (b), the tin alkoxide reacted with L-lactide generating a linear monomer and starting



propagation step. The polymer was growing to high molecular weight until the active site was no longer active. The chain ends of PLLA were benzyl and hydroxyl groups.



**Scheme 4.2** Mechanism of synthesis of linear PLLA prepolymer with the ROP method: tin alkoxide forming (a), and propagation of PLLA chain (b).

Figure 4.1 shows an  $^1\text{H}$  NMR spectrum of BA (1) and the linear PLLA (2), The proton signals at 1.58 and 5.18 ppm were assigned to methyl and methine protons of lactide unit, respectively. In addition, the solf signal at 7.38 ppm was also assigned to the proton of benzene ring (of BA) at the chain end of PLLA. The proton signals of BA at 4.65 ppm did not appear in the spectrum of PLLA indicating that BA was removed from the PLLA product.

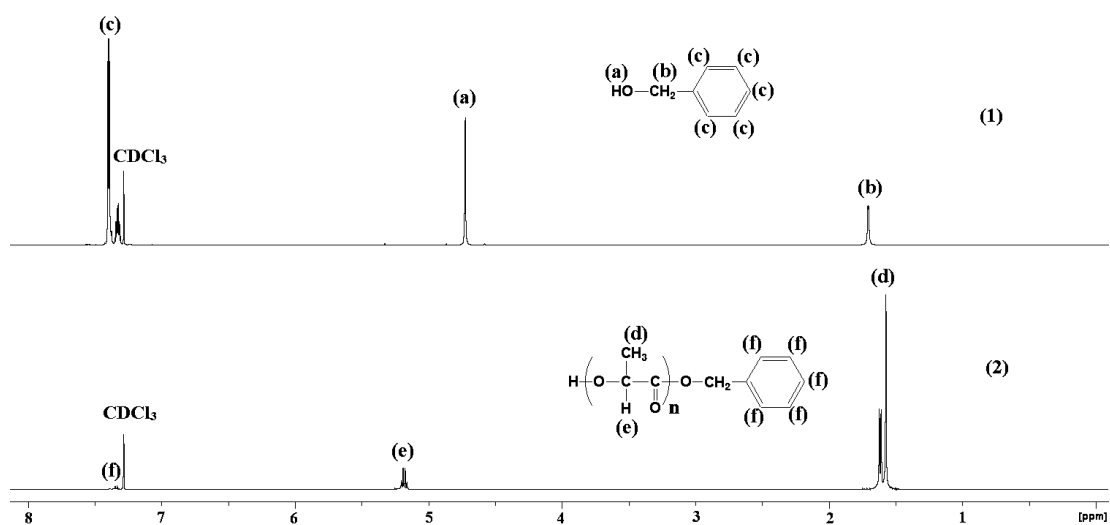


Figure 4.1  $^1\text{H}$  NMR spectra of BA (1) and the linear PLLA (L4) (2).

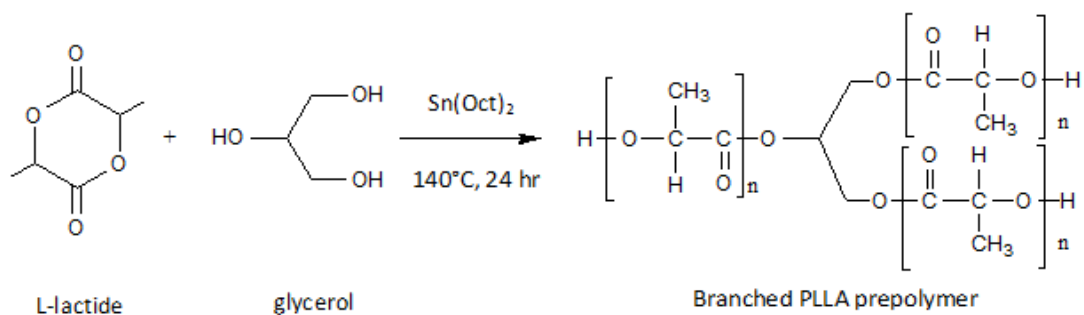
Table 4.1 shows the molecular weight, dispersity, and yield of PLLA varying mole ratio of BA and the molar ratio of initiator/monomer.  $\bar{M}_n$  was determined by GPC. It was observed that the  $\bar{M}_n$  of linear polymers increased with increasing the monomer ratios from 1/80 to 1/250. A similar trend was also observed from the theoretical  $\bar{M}_n$ . However, the  $\bar{M}_n$  was slightly lower than the theoretical value because the crude product was rigid before the reaction is complete. Chain mobility and probability of molecular attack (at the chain end) must be taken into account. The yields of products are rather high.

**Table 4.1** Molecular weight, dispersity, and yield of linear PLLA prepolymer synthesized by varying molar ratio of initiator/monomer.

Sample code	BA/LLA (mol/mol)	$\bar{M}_n$ (GPC) (g/mol)	$\bar{M}_n$ (Theo) (g/mol)	Dispersity	Yield
L1	1/80	10,480	11,530	1.22	72
		11,014	11,530	1.42	80
		13,066	11,530	1.32	81
		9,245	11,530	1.45	72
		12,421	11,530	1.31	72
L2	1/150	20,793	21,600	1.41	69
L3	1/200	29,834	28,800	1.11	71
L4	1/250	34,890	36,000	1.21	74
L5	1/350	38,011	50,443	1.24	75

#### 4.1.2 Synthesis of branched PLLA prepolymer

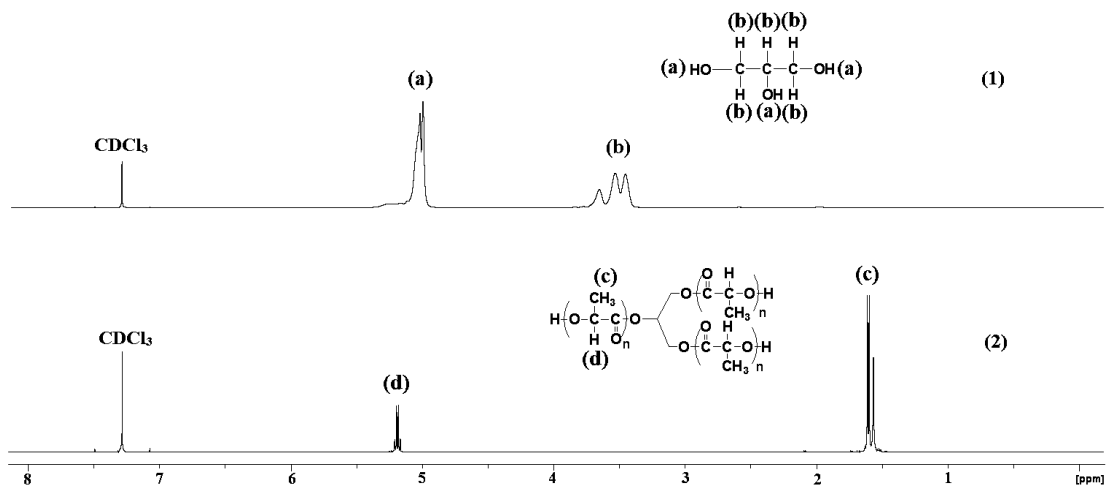
Branched PLLA prepolymer was synthesized by ROP of L-lactide as monomer with glycerol as initiator as shown in Scheme 4.3.



**Scheme 4.3** Synthesis of branched PLLA prepolymer from L-lactide.

Figure 4.2 shows an  $^1\text{H}$  NMR spectra of GL (1) and the branched PLLA (2), The proton signals at 1.58 and 5.18 ppm were assigned to methyl and methine protons of lactide unit, respectively. The proton signals of GL at 3.45-3.70 and 5.1 ppm were belonging to methane and methylene groups, and hydroxyl group, respectively. For the branched PLLA, the signal at 4.2 ppm belonging to the methylene groups of

glycerol in the PLLA chain did not, however, appear in the spectrum of PLLA, probable due to its intensity was too low to be visible.



**Figure 4.2**  $^1\text{H}$  NMR spectra of GL (1) and the branched PLLA (B4) (2)

The molecular weight, dispersity, and yield of branched PLLA after varying mole ratio of GL and initiator/monomer are shown in Table 4.2. It was observed that the  $\bar{M}_n$  of branched polymers increased with increasing the monomer ratios from 1/80 to 1/250. At the higher monomer ratio, the  $\bar{M}_n$  did not increase as predicted in the theoretical values. This could be explained by the fact that propagation in branched structures somewhat retarded by the steric hindrance of the nearby polymer chains. The yields of products are rather high.

**Table 4.2** Molecular weight, dispersity, and yield of branched PLLA prepolymer synthesized by varying molar ratio of initiator/monomer.

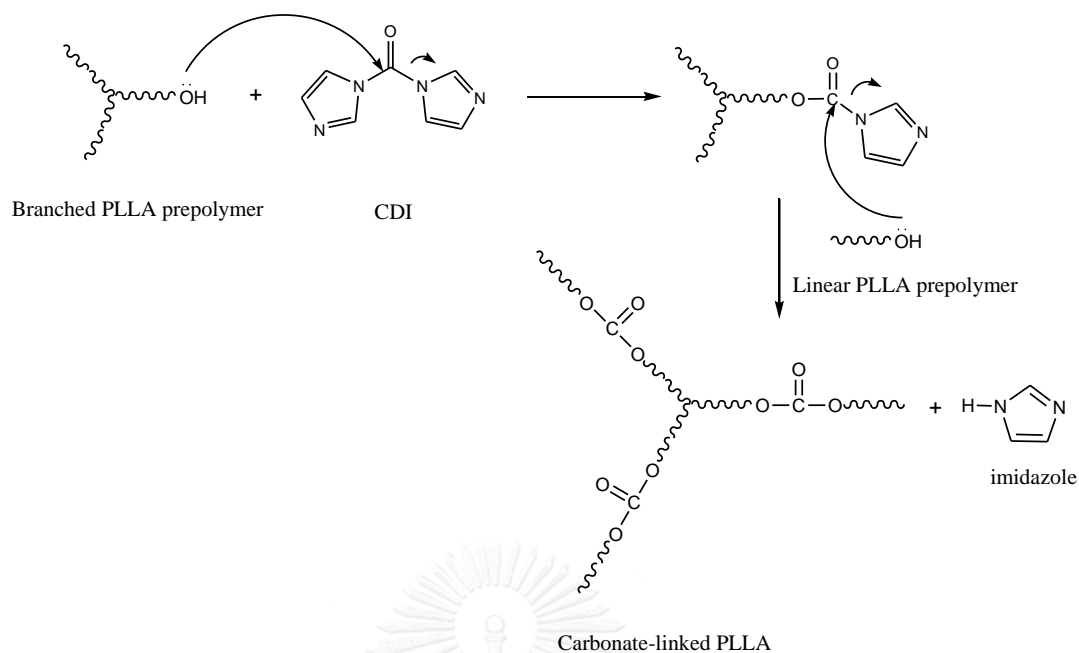
Sample code	GL/LLA (mol/mol)	$\bar{M}_n$ (GPC) (g/mol)	$\bar{M}_n$ (Theo) (g/mol)	Dispersity	Yield
B1	1/80	11,276	11,530	1.81	65
		12,714	11,530	2.08	71
		12,866	11,530	2.01	82
		13,245	11,530	1.91	76
B2	1/150	22,479	21,600	1.89	74
B3	1/200	25,281	28,800	1.48	75
B4	1/250	26,114	36,000	1.47	81

## 4.2 Chain extension of branched PLLA prepolymer

In this section, attempts to increase the molecular weight of branched prepolymer were carried out by connecting the linear and branched PLLA prepolymers with selected coupling agents in solution. The role of chain extender was to join two hydroxyl ends of two polymer chains together. The mole ratios of branched chain to linear chain was fixed at 1:3 and the molecular weight of prepolymer was about 10,000 g/mol. The two types of chain extender used in this study were hexamethylene diisocyanate (HDI) and 1,1'-carbonyl diimidazole (CDI).

### 4.2.1 CDI as chain extender

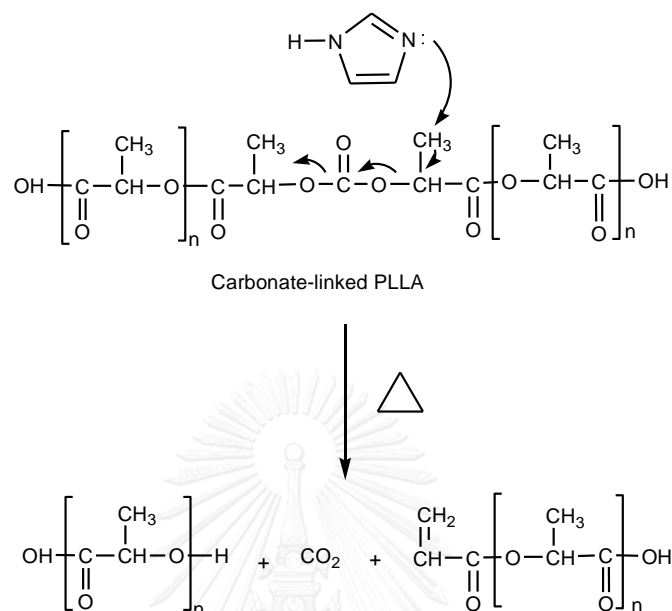
Scheme 4.4 shows the reaction of PLLA prepolymer with CDI. The CDI molecule joins each hydroxyl group of the prepolymer to form carbonate-linked PLLA. The obtained branched PLLA after reaction had high molecular weight [36].



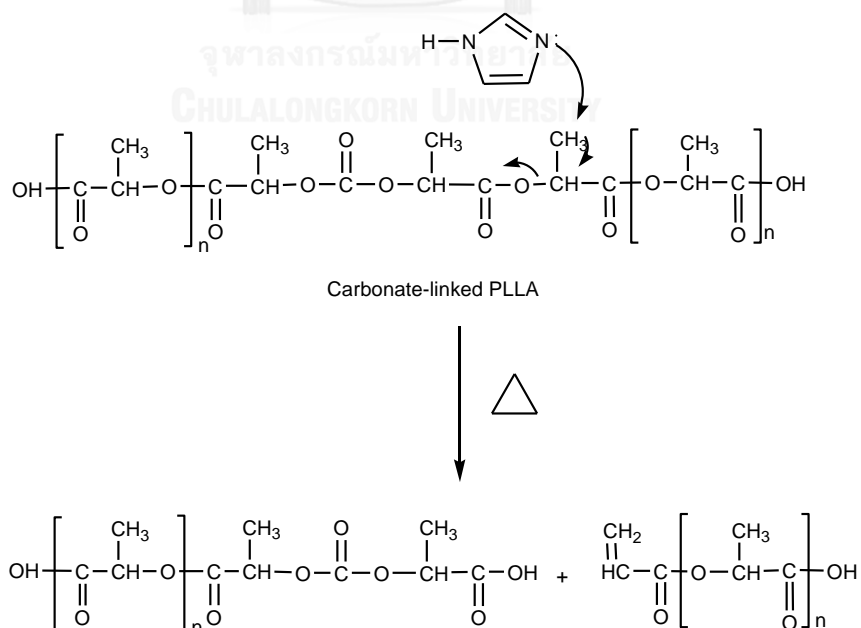
**Scheme 4.4** Mechanism of chain extension by joining two hydroxyl groups of PLLA chains, forming carbonate bond.

Table 4.3 shows effect of mole ratios of branched: linear PLLA prepolymer: CDI, The mole ratio of 3-arm branched to linear chains was fixed at 1 to 3, and the  $\bar{M}_n$  of the prepolymer was about 10,000 g/mol. Increasing the mole ratio of chain extender (CDI1-4) led to a slight increase of  $\bar{M}_n$ , from 14,000-19,000 g/mol. These results were lower than what would expect (40,000 g/mol) after three linear chains attached to the 3-arm branched polymer. This result suggested that the possibility of having two chain ends reacted with the chain extender molecule, was rather low. Using xylene as the solvent to increase mixing of all reactants was not quite adequate. Increasing the reaction time from 0.5 to 20 hr (CDI5-8) did not improve the coupling process. It was possible after more than 5 hr transesterification took place and resulted in MW decreasing. It is also possible that, the imidazole by-product could cause the decrease the  $\bar{M}_n$  by subtracting a proton of the methyl group in the lactide unit adjacent to the newly formed carbonate bond. The mechanism of carbonate cleavage and ester cleavage are proposed in Scheme 4.5 and 4.6 [18]. For increasing the  $\bar{M}_n$  of linear PLLA, 20,000 to 35,000 g/mol, the  $\bar{M}_n$  of polymer product

was not change. In addition, the molecular weight distribution was high when the molecular weights of prepolymer were highly different.



**Scheme 4.5** Fragmentation of PLLA by the abstraction of proton by imidazole at the methyl group in the unit adjacent to the newly formed carbonate bond.



**Scheme 4.6** Fragmentation of PLLA by the abstraction of proton by imidazole at the methyl group in the lactide repeat unit.

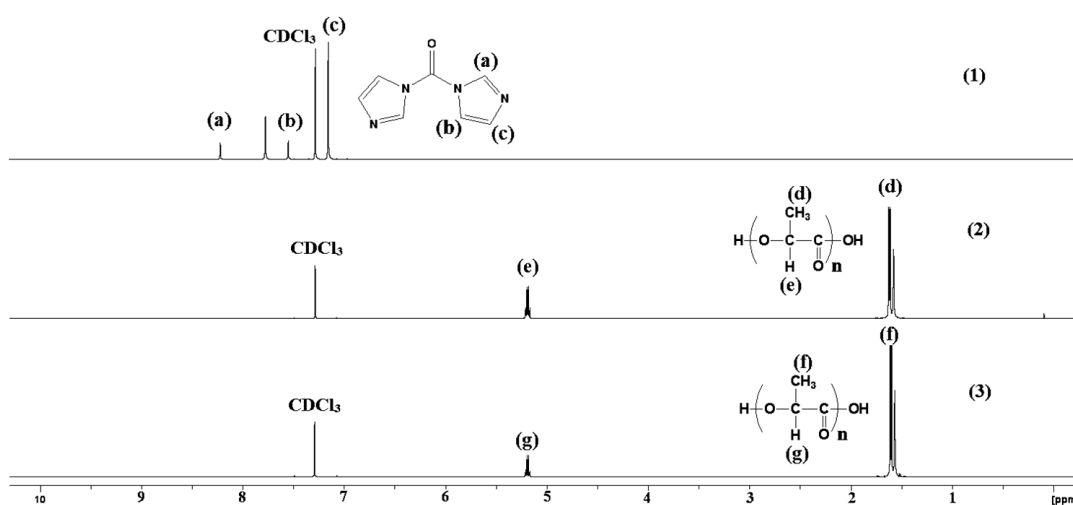
**Table 4.3** Molecular weight, dispersity, and yield of branched PLLA in the presence of CDI as chain extender, solvent:xylene, T= 110°C.

Sample code	Before reaction with CDI				After reaction with CDI		
	$\bar{M}_n$ of linear PLLA (g/mol)	$\bar{M}_n$ of branched PLLA (g/mol)	Molar ratio of B/L/CDI <sup>1</sup>	Rxn time (h)	$\bar{M}_n$ of PLLA product (g/mol)	Dispersity	Yield (%)
PLLA-pre	11,014	11,276	1/3/0	3	9840	1.29	80
CDI1	11,014	11,276	1/3/3	3	13,811	1.31	79
CDI2	11,014	11,276	1/3/6	3	15,349	1.21	83
CDI3	9,245	12,741	1/3/9	3	17,224	1.22	76
CDI4	11,014	11,276	1/3/12	3	19,144	1.40	76
CDI5	13,066	11,276	1/3/6	0.5	13,911	1.21	72
CDI6	13,066	11,276	1/3/6	5	16,418	1.32	62
CDI7	13,066	12,714	1/3/6	10	14,186	1.24	61
CDI8	9,245	12,714	1/3/6	20	10,016	2.01	65
CDI8-Re	9,245	12,714	1/3/6	20	12,473	1.31	78
CDI9	20,793	12,866	1/3/6	3	15,014	1.69	84
CDI10	29,834	12,866	1/3/6	3	16,171	1.34	74
CDI12	20,793	12,866	1/3/9	3	14,441	1.27	71
CDI13	29,834	12,866	1/3/9	3	5,152	1.14	64
					19,957	1.15	
CDI14	38,011	12,866	1/3/9	3	16,412	1.21	78
					25,411	1.37	

<sup>1</sup>B/L/CDI = branched/linear/CDI

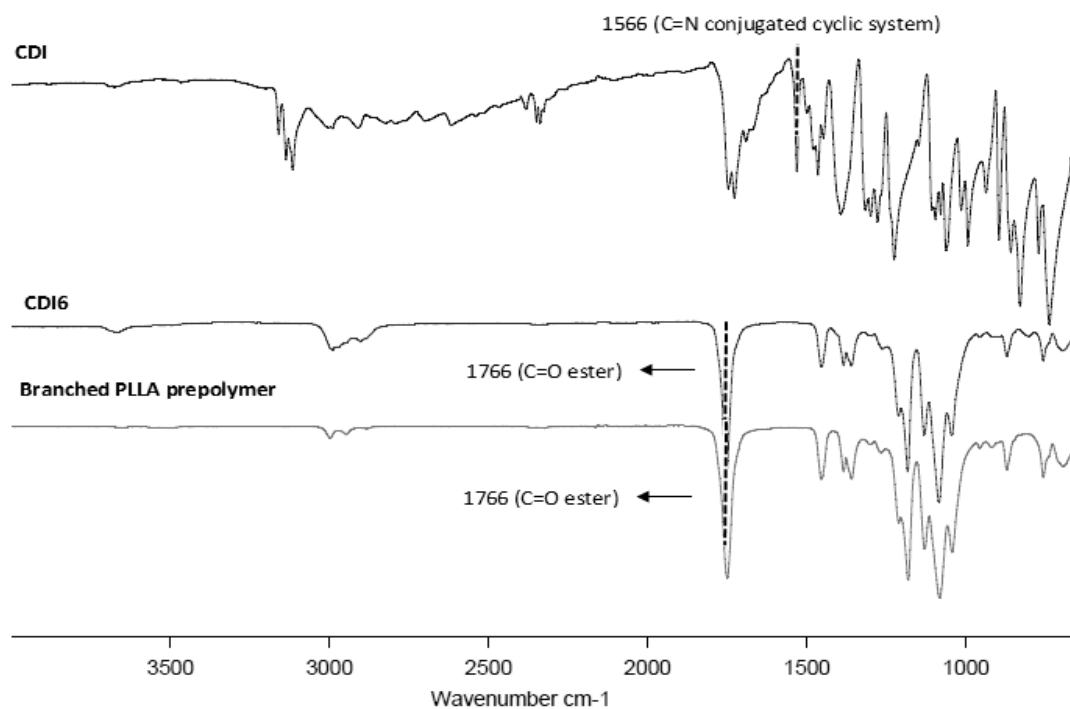


Figure 4.3 shows the  $^1\text{H}$  NMR spectra of CDI, CDI10, and branched PLLA prepolymer. The proton signals at 1.59 and 5.20 ppm were assigned to methyl and methine protons of lactide unit, respectively. The proton signals of CDI at 7.26, 7.55 and 8.20 ppm were no appear in the spectrum of PLLA product (CDI10). This indicated that CDI and imidazole were removed from the PLLA product.



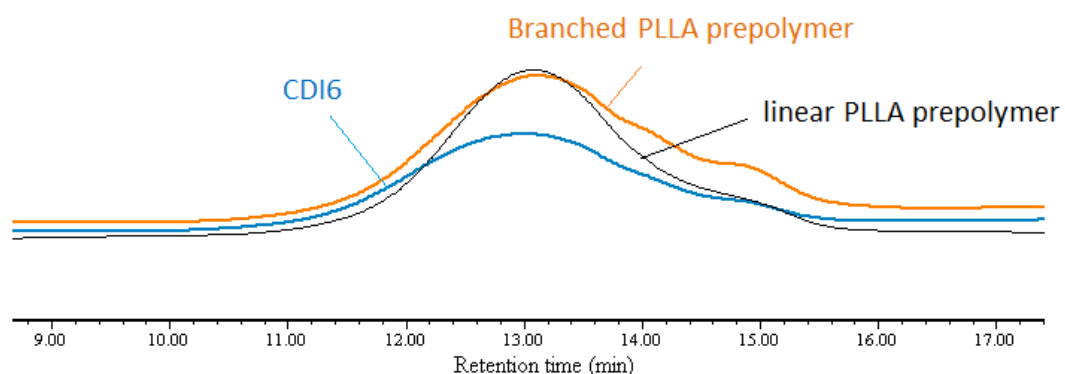
**Figure 4.3**  $^1\text{H}$  NMR spectra of CDI (1), and the CDI10 (2) (after chain extension reaction), and branched PLLA prepolymer (3) in  $\text{CDCl}_3$ .

Figure 4.4 show the FTIR spectra of CDI, CDI6, and branched PLLA prepolymer. The peak at  $1766\text{ cm}^{-1}$  assigned to  $\text{C}=\text{O}$  of ester group in the PLLA chain. For CDI, appearance of a peak at  $1566\text{ cm}^{-1}$  assigned to  $\text{C}=\text{N}$  conjugated cyclic system. This peak did not appear in PLLA product (CDI6). This result was consistent with the result of  $^1\text{H}$  NMR, indicating that imidazole was removed from the PLLA product.



**Figure 4.4** FTIR spectra of CDI, CDI6, and branched PLLA prepolymer.

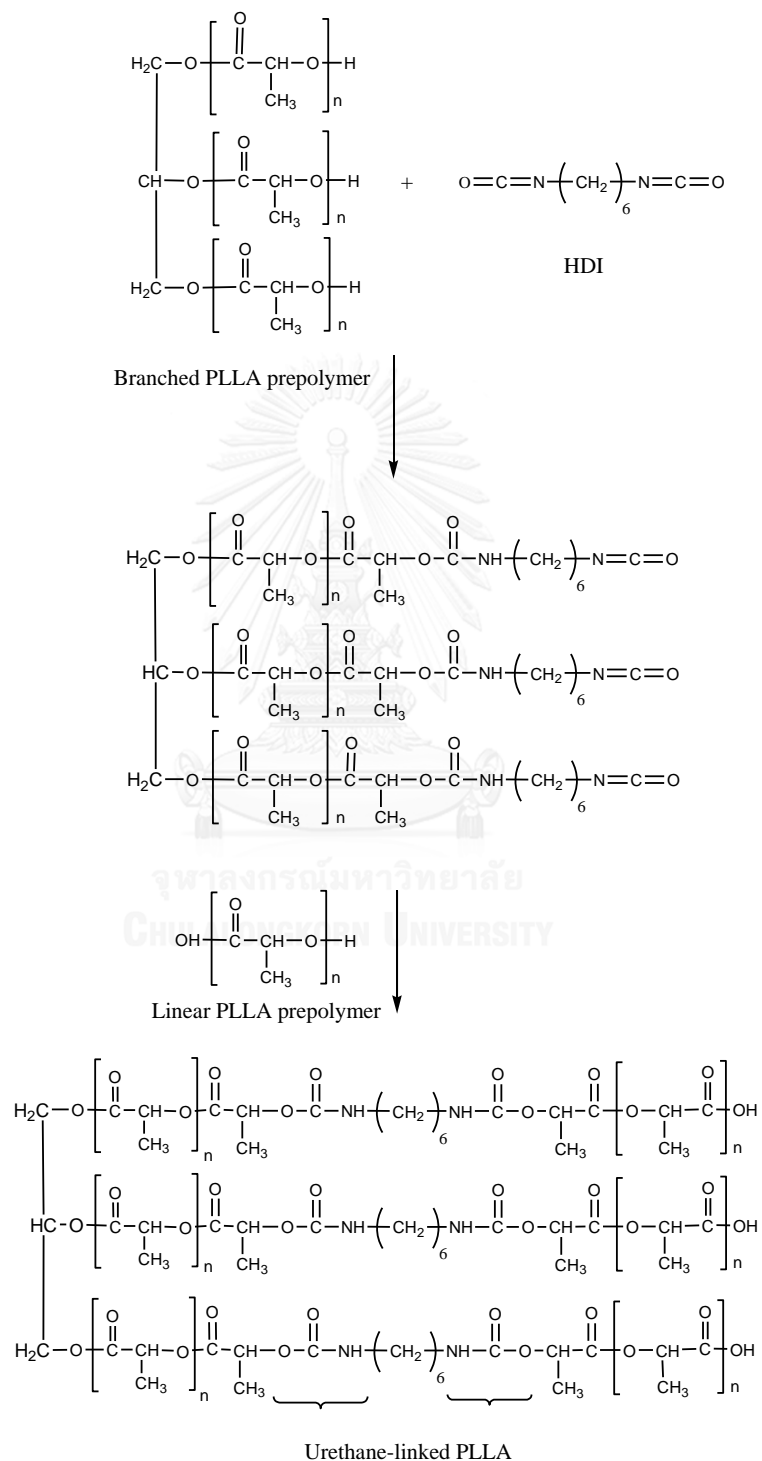
Figure 4.5 shows GPC chromatograms of CDI6 and the PLLA prepolymers. The chromatogram of CDI6 shows a small high molecular weight peak comparing with the PLLA prepolymer.



**Figure 4.5** The GPC chromatogram of CDI6, branched PLLA prepolymer, and linear PLLA prepolymer.

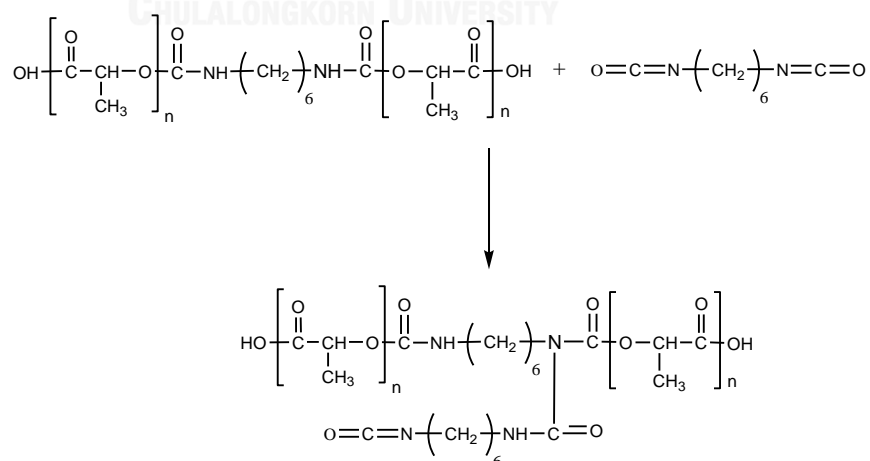
#### 4.2.2 HDI as chain extender

The hydroxyl end-groups of two prepolymers could react with the isocyanate end-groups of HDI to form new urethane linkages as shown in scheme 4.7.



**Scheme 4.7** The reaction of hydroxyl terminal group (-OH) of PLLA prepolymer with HDI as chain extender.

Table 4.4 shows the effect of HDI chain extender in several reaction conditions. The mole ratio of branched to linear chains was fixed at 1 to 3 and the molecular weights of prepolymers were about 10,000 g/mol. When the molar ratio of HDI was increased from 3 to 12 times of the branched structure (sample HDI1-HDI5), the  $\bar{M}_n$  increased as planned. But when HDI was added as high as 15 times, its  $\bar{M}_n$  surprisingly dropped. This suggests that too many HDI molecules would react with all hydroxyl end groups, forming to be crosslinking or branching by allophanate reaction, reaction of -NCO with urethane as shows in Scheme 4.8. The one brought about to leaving no free hydroxyl groups to join in the extension process. It was observed from the increasing of gel content. Considering the reaction, increasing the reaction time from 0.5-5 hr (HDI6-9), led to increases in the molecular weight of PLLA. At reaction time more than 5 hr, the molecular weight of products decreased because polymer was degraded by transesterification reaction with heating. For increasing the molecular weight of prepolymer from 10,000 to 20,000 g/mol, the molecular weight of final product increased, but decreased when  $\bar{M}_n$  of linear PLLA was more than 20,000 g/mol. It was probably because the viscosity of the reaction mixture increased when added the high molecular weight prepolymer. Therefore, the possibility of having two chain ends to react with the chain extender molecule was low.



**Scheme 4.8** Allophanate reaction, the reaction of -NCO and urethane to form the crosslinking or branching of PLLA product.

**Table 4.4** Molecular weight, dispersity, yield, and gel content of branched PLLA in the presence of HDI as chain extender, solvent:xylylene, T= 110°C.

Sample code	Before reaction with HDI				After reaction with HDI			
	$\bar{M}_n$ of linear PLLA (g/mol)	$\bar{M}_n$ of branched PLLA (g/mol)	Molar ratio of B/L/HDI <sup>1</sup>	Rxn time (h)	$\bar{M}_n$ of PLLA product (g/mol)	Disper-sity	Yield (%)	Gel content (%)
PLLA-pre	10,480	11,276	1/3/0	3	10,977	1.44	74	2.4
HDI1	10,480	11,276	1/3/3	3	23,441	1.73	89	2.5
HDI2	10,480	11,276	1/3/6	3	37,412	1.78	84	3.4
HDI3	9,245	11,276	1/3/9	3	48,411	1.53	86	2.3
HDI4	11,014	12,714	1/3/12	3	52,455	2.01	89	5.5
HDI5	11,014	12,866	1/3/15	3	46,719	1.54	76	5.8
HDI6	11,014	12,714	1/3/6	0.5	25,196	1.51	80	3.1
HDI7	11,014	12,714	1/3/6	5	41,441	1.24	80	3.2
HDI8	11,014	12,866	1/3/6	10	37,427	1.45	88	3.4
HDI9	13,066	12,866	1/3/6	20	35,670	1.18	86	3.1
HDI10	20,793	12,866	1/3/6	3	54,424	1.79	79	2.6
HDI11	29,834	12,866	1/3/6	3	41,441	1.17	88	3.2
HDI12	34,890	12,866	1/3/6	3	39,778	2.00	87	3.6

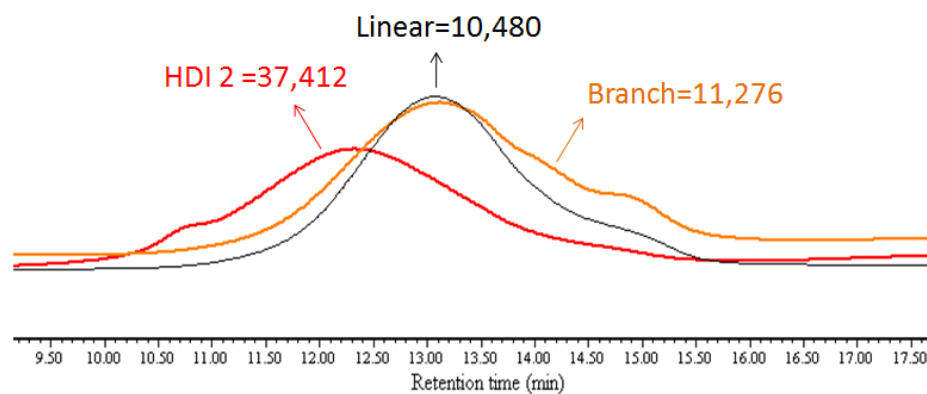
<sup>1</sup>B/L/HDI = branched/linear/HDI

**Table 4.5 (Continued)** Molecular weight, dispersity, yield, and gel content of branched PLLA in the presence of HDI as chain extender, solvent:xylene, T= 110°C.

Sample code	Before reaction with HDI				After reaction with HDI			
	$\bar{M}_n$ of linear PLLA (g/mol)	$\bar{M}_n$ of branched PLLA (g/mol)	Molar ratio of B/L/HDI <sup>1</sup>	Rxn time (h)	$\bar{M}_n$ of PLLA product (g/mol)	Dispersity	Yield (%)	Gel content (%)
HDI13	20,793	13,245	1/3/9	3	49,477	2.11	89	3.1
HDI14	29,834	13,245	1/3/9	3	48,941	2.47	82	5.1
HDI15	34,890	12,714	1/3/9	3	45,534	2.30	85	3.6

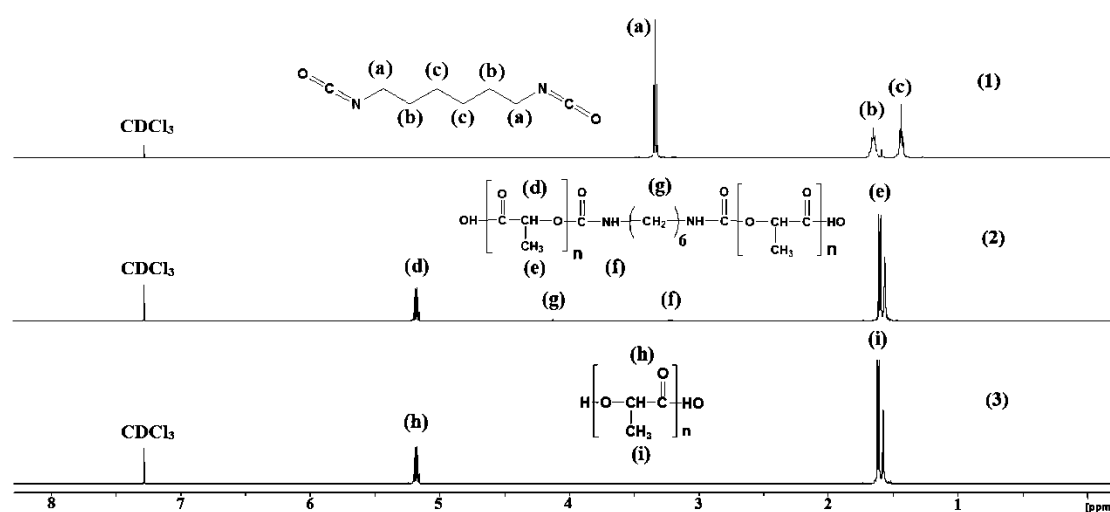
<sup>1</sup>B/L/HDI = branched/linear/HDI

Figure 4.6 shows GPC chromatogram of HDI2 and PLLA prepolymer. The chromatogram of HDI2 shows a small high molecular weight shoulder (around 10.7 min), indicating very high mass polymers ( $\bar{M}_n=114,470$  g/mole), such as crosslinking between two or more branched structures could be obtained by this HDI coupling method.



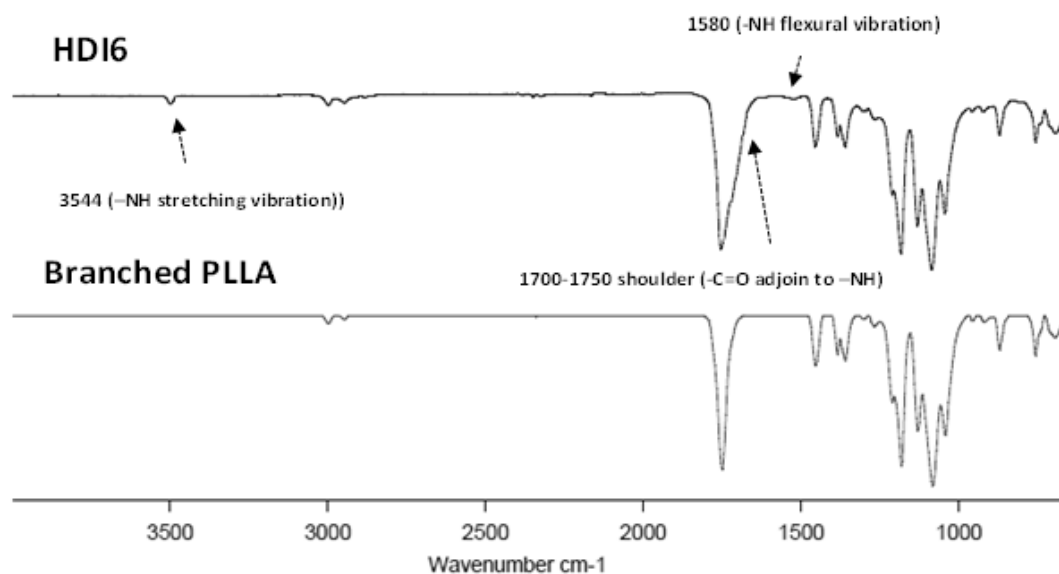
**Figure 4.6** The GPC chromatograms of HDI2, branched PLLA prepolymer, and linear PLLA prepolymer.

Figure 4.7 shows the  $^1\text{H}$  NMR spectra of HDI, HDI5, and branched PLLA prepolymer. The proton signals at 1.59 and 5.20 ppm were assigned to methyl and methine protons of lactide unit, respectively. The proton signals of HDI at 1.46, 1.68 and 3.34 ppm were no appear in the spectrum of PLLA product (HDI5). The spectrum of HDI5 appeared signals of 3.28 and 4.18 ppm, which were assigned to the unit of HDI connecting between two chain ends of prepolymer.



**Figure 4.7**  $^1\text{H}$  NMR spectra of HDI (1), and the HDI5 (2) (after chain extension reaction), and branched PLLA prepolymer (3) in  $\text{CDCl}_3$ .

Figure 4.8 shows the FTIR spectra of HDI5 and branched PLLA prepolymer. The spectra of HDI5, appearances of a peak at  $1580\text{ cm}^{-1}$  assigned to  $-\text{NH}$  flexural vibration, a shoulder at  $1700\text{--}1750\text{ cm}^{-1}$  assigned to  $-\text{C}=\text{O}$  adjoin to  $-\text{NH}$ , and a peak at  $3544\text{ cm}^{-1}$  assigned to  $-\text{NH}$  stretching vibration. This result indicated that HDI reacted with the chain ends of prepolymer.



**Figure 4.8** FTIR spectra of CDI6 and branched PLLA prepolymer.

Figures 4.9 and 4.10 show the DSC thermogram of PLLA prepolymer and the PLLA polymer after chain-extension with HDI at cooling and 2<sup>nd</sup> heating. In the cooling scan,  $T_{cc}$  increased with increasing molecular weight. It was similar to its crystallinity. This indicated that the high mobility of short chain length retarded to opportunity of chain packing to form crystal. In the 2<sup>nd</sup> heating scan,  $T_g$  was not observed probably because the polymer had high crystal from the cooling step. The  $T_m$  increased when increasing its molecular weight. However, the crystallinity at  $T_m$  was higher than at  $T_{cc}$ . It was expected that having some part of crystal generated during heating in the 2<sup>nd</sup> step, forming to cold crystallization before melting at  $T_m$  in which the DSC machine was not measure the one. Table 4.5 shows all thermal analysis results.



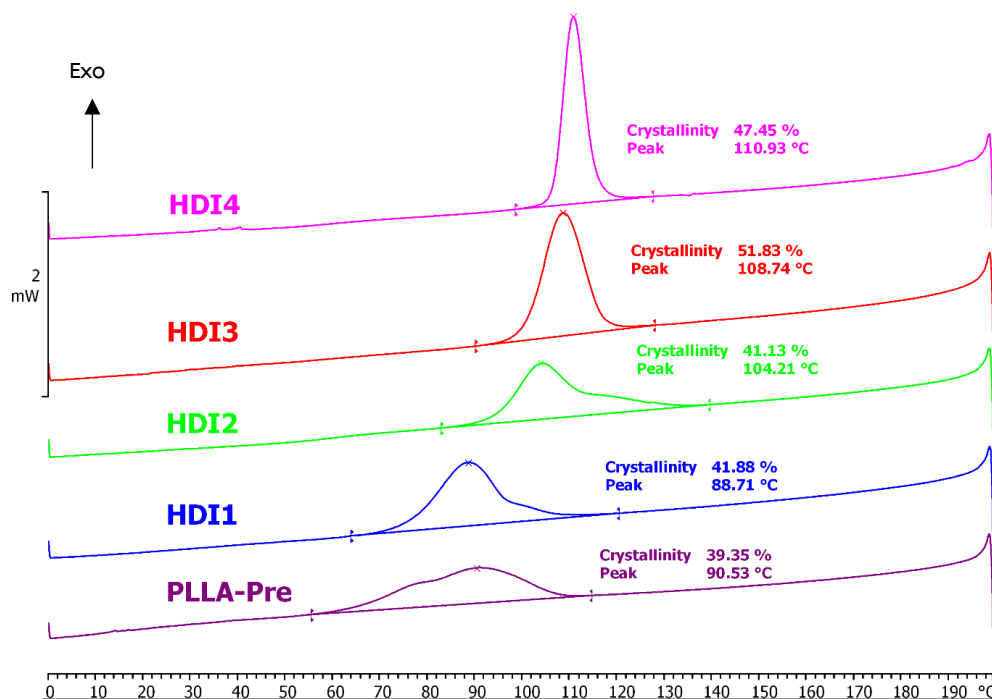


Figure 4.9 DSC thermograms at cooling step of second heat of PLLA prepolymer and the PLLA polymer after extension with HDI at cooling rate 10°C, N<sub>2</sub> atmosphere.

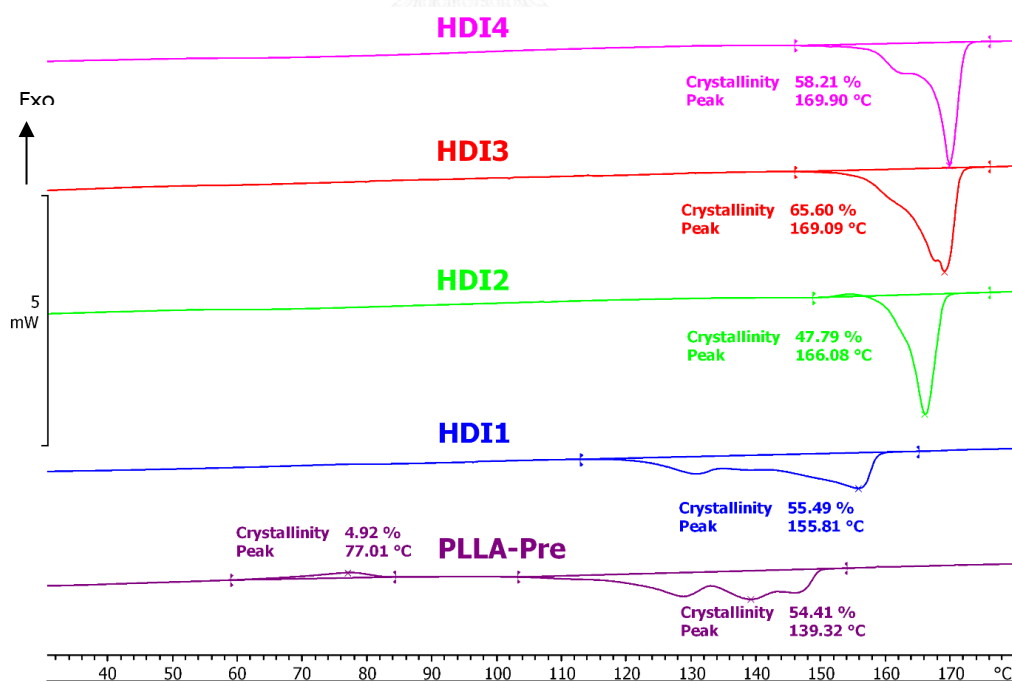
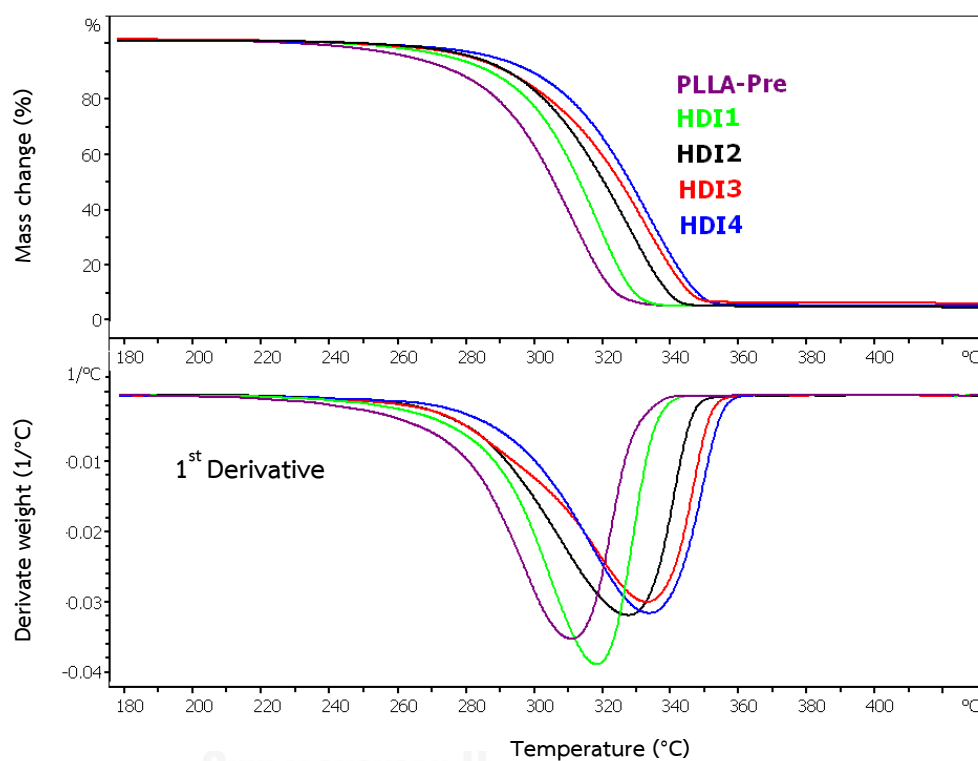


Figure 4.10 DSC thermograms at 2<sup>nd</sup> heat of PLLA prepolymer and the PLLA polymer after extension with HDI at heating rate 10°C, N<sub>2</sub> atmosphere.

Figure 4.11 shows the TGA curves of PLLA prepolymer and the PLLA polymer after extension with HDI. Degradation temperature ( $T_d$ ) increased when increasing molecular weight of PLLA polymer. It can be explained that, the low molecular weight PLLA had much more hydroxyl groups at the chain end, the hydroxyl group led to fast degradation of PLLA by transesterification reaction.



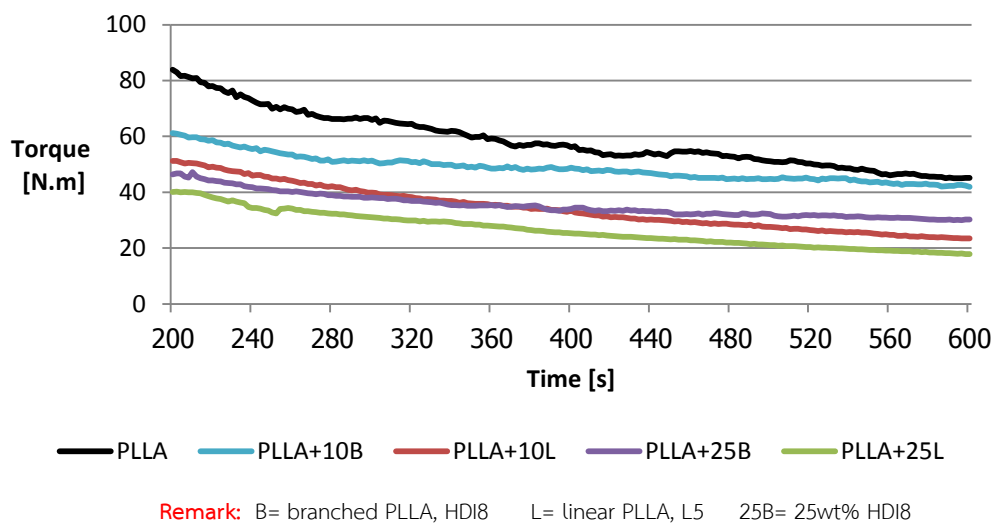
**Figure 4.11** TGA curves of PLLA prepolymer and the PLLA polymer after extension with HDI.

**Table 4.6** Thermal properties of PLLA prepolymer and the PLLA polymer after extension with HDI at heating rate 10°C, N<sub>2</sub> atmosphere.

Sample	Cooling		2 <sup>nd</sup> Heating		TGA	
	T <sub>cc</sub> (°C)	X <sub>cc</sub> (%)	T <sub>ch</sub> (°C)	X <sub>m</sub> (%)	Onset (°C)	T <sub>d</sub> (°C)
PLLA-pre	90.53	39.53	139.32	54.41	279.11	310.88
HDI1	88.71	41.88	155.81	55.49	291.42	319.21
HDI2	104.21	41.13	166.08	47.79	301.12	329.22
HDI3	108.74	51.83	169.09	65.60	309.18	337.00
HDI4	110.93	47.45	169.90	58.21	314.12	338.83

### 4.3 Blending of linear and long-chain branched PLLA, and melt strength testing

Figure 4.12 shows the corresponding torque and temperature of linear and long-chain branched PLLA blending with commercial PLLA (3251D) in internal mixer. PLLA grade 3251D ( $\bar{M}_n=120,000$  g/mol) from Nature Work was blended with synthesized PLLA, linear and branched PLLA (L5 and CD18), fixed the  $\bar{M}_n$  as 38,000 g/mol. The content of added synthesized PLLA was varied at 10 and 25 wt%. It was found that when adding low  $\bar{M}_n$  PLLA, torque decreased. However, the one with the 3-arms branched PLLA had a high torque, compared with linear PLLA. A similar trend was also observed from the melt strength result as shown in Table 4.6. It can postulated that branched PLLA increased viscosity with the entanglement of polymer, leading to high melt strength.



**Figure 4.12** The corresponding torque and temperature of linear and long- chain branched PLLA blending with commercial PLLA(3251D) in internal mixer at 190°C, 40 rpm, and 10 min.

**Table 4.7** Melt strength of the obtained PLLA product after blending in internal mixer.

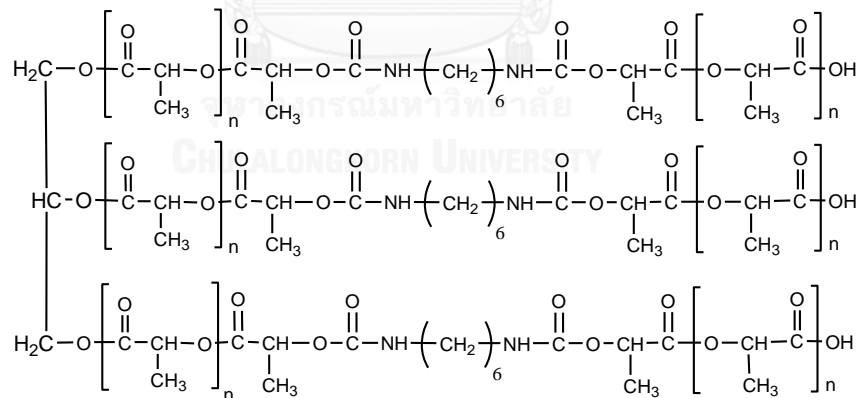
Sample	Melt strength (cN)
PLLA (grade 3251D)	9.1
PLLA+10L	6.2
PLLA+25L	5.7
PLLA+10B	7.0
PLLA+25B	6.2

## CHAPTER 5

### CONCLUSION

#### 5.1 Conclusion

High molecular weight branched PLLAs were synthesized by using chain extender molecule. In the first step, linear and 3-armed branched PLLA were synthesized via ROP method. In the second step, the length of each arm was extended by joining with the linear PLLA chains via the terminal hydroxyl groups using chain extender. Two types of chain extenders were studied: 1,1'-carbonyl diimidazole (CDI) and hexamethylene diisocyanate (HDI). CDI was found to be inferior to HDI in terms of  $\bar{M}_n$  increase. This was because effect of chain fragmentation happened during reaction by imidazole by-product. The maximum  $\bar{M}_n$  of extended 3-arm branched PLLA was 54,000 g/mol when HDI was used as the chain extender. However, high dosed HDI led to an increase of gel content by undesired allophanate formation.



**Scheme 5.1** The 3-arm branched PLLA after chain extension with HDI.

High  $\bar{M}_n$  branched PLLA formed better crystal compare with low  $\bar{M}_n$ . In addition, the high  $\bar{M}_n$  was also rather slow degradation. Because it had low hydroxyl group, which led to transesterification reaction. The melt strength of PLLA was improved by adding branched PLLA, increased to entanglement of polymer chain. Therefore, the problem of processing was improved.

## 5.2 Future Direction

In this work, the chain extending molecules were utilized in a chemical reaction setup. This could face some difficulties in scale-up operation. A further study that is concentrated in scaling up is needed.



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## VITA

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