CHAPTER 2

EXPERIMENTAL METHODS

2.1 Chemicals, Apparatus and Instruments

2.1.1 Chemicals

The various chemicals used in this research project were listed in Table 2.1.

Table 2.1 Chemicals used in this research project.

Chemical	Usage	Supplier	Grade
1. L-Lactic acid, $C_3H_6O_3$	Monomer Precursor	Carlo Erba	88 %
2. ε-Caprolactone, $C_6H_{10}O_2$	Monomer	Acros	99 %
3. Tin chloride anhydrous, $SnCl_2$	Catalyst Precursor	Acros	98 %
4. Diethylamine, $HN(C_2H_5)_2$	Catalyst Precursor	PS, Panreac	99.5 %
5. n-Butanol, C_4H_9OH	Catalyst Precursor	Lab-Scan	99.4 %
6. Stannous octoate, $C_{16}H_{30}O_4Sn$	Catalyst	Sigma Chemicals	95 %
7. 1-Hexanol, $C_6H_{13}OH$	Initiator	Fluka AG	≥ 98 %
8. n-Heptane, $CH_3(CH_2)_5CH_3$	Solvent	BDH Chemicals	99.5 %
9. Ethyl acetate, $CH_3COOC_2H_5$	Solvent	ICI	commercial
10. Acetone, C_3H_6O	Solvent	BDH Chemicals	AR grade
11. Methanol, CH_3OH	Solvent	BDH Chemicals	AR grade
12. Chloroform, $CHCl_3$	Solvent	BDH Chemicals	AR grade
13. d_6-Chloroform, $CDCl_3$	Solvent	Aldrich	AR grade
14. Tetrahydrofuran, C_4H_8O	Solvent	SK Chemicals	99.8 %
15. Orthophosphoric acid, H_3PO_4	Heating Bath	Carlo Erba	85 %

Table 2.1 continued

Chemical	Usage	Supplier	Grade
16. Calcium hydride, CaH_2	Drying agent	Carlo Erba	≥ 95 %
17. Molecular sieves 4 Å	Drying agent	Aldrich	Commercial

2.1.2 Apparatus and Instruments

The main items of apparatus and instruments used were listed in Table 2.2.

Table 2.2 Apparatus and instruments used in this research project.

Apparatus and Instruments	Company	Model
1. Vacuum Desiccators	-	Gallenkamp
2. Vacuum Oven	Fisher Scientific	282 A
3. Vacuum Pump	BOC Edwards	Edwards Model RVR
4. Controlled Atmosphere Glove Box	Labconco	50004
5. Rotary Evaporator	Buchi	R-200
6. FT-IR Spectrometer	Bruker	TENSOR 27
7. ^{1}H-NMR Spectrometer	Bruker	Avace 400
8. ^{13}C-NMR Spectrometer	Bruker	Avace 400
9. Gel Permeation Chromatograph	Waters	2414
10. Differential Scanning Calorimeter	Perkin-Elmer	DSC 7
11. Thermogravimetric Analyzer	Perkin-Elmer	TGA 7
12. Universal Mechanical Testing Machine	Lloyd Instruments	LRX+
13. Automatic Viscosity Measuring System	Schott-Gerate	AVS300
14. Parr Reactor	Parr Instruments	4520
15. Dynamic Mechanical Analyzer	Mettler Toledo	DMA/SDTA 861^e

Table 2.2 continued

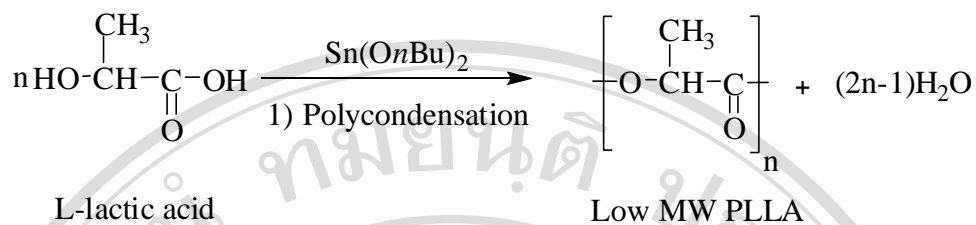| Apparatus and Instruments	Company	Model
16. Rotational Rheometer	Malvern	Bohlin Germini HR^{nano}
17. Scanning Electron Microscope	JOEL	JSM-5910LV
18. Small Scale Melt Spinning Apparatus	Bradford University Research	-

2.2 Materials

2.2.1 Monomer Preparation and Purification

The cyclic ester monomers used in this research project were L-lactide (LL) and ε-caprolactone (CL). Since L-lactide is prohibitively expensive to buy (4,320 baht/25g) [60], it was synthesized in our laboratory from its much cheaper precursor, L-lactic acid. The method of synthesis and purification are described in the following sections 2.2.1.1 and 2.2.1.3. ε-Caprolactone is more readily available and was purchased for use in this research project. However, this commercially available monomer may contain a number of impurities or additives that must be carefully removed prior to use as described in section 2.2.1.5. The purity of monomers has an important influence on its subsequent polymerisability.

2.2.1.1 Synthesis of L-Lactide

The synthesis of L-lactide is a two-step reaction involving, firstly the linear polycondensation of L-lactic acid to low molecular weight poly(L-lactic acid) (PLLA) followed, secondly by thermal decomposition of the PLLA to yield L-lactide as the primary decomposition product, as shown below.

Step 1: Linear polycondensation of L-lactic acid to low molecular weight PLLA

$$n\ \text{HO-CH-C-OH} \xrightarrow[\text{1) Polycondensation}]{\text{Sn(O}n\text{Bu)}_2} \left[\text{O-CH-C} \right]_n + (2n\text{-}1)\text{H}_2\text{O}$$

L-lactic acid   Low MW PLLA

Step 2: Thermal decomposition of low molecular weight PLLA to L-lactide

$$\left[\text{O-CH-C} \right]_n \xrightarrow{\text{2) Thermal decomposition}} \text{L-lactide}$$

Low MW PLLA   L-lactide
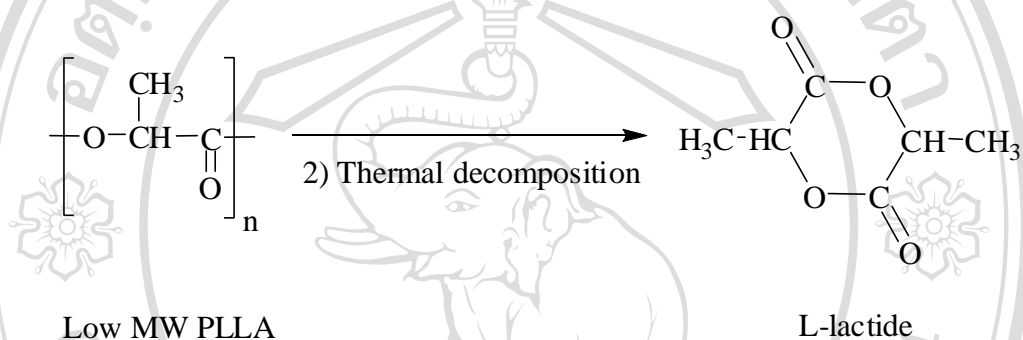
    In a typical synthesis reaction in this experiment, approximately 1000 g of L-lactic acid were added into a 1000 ml round-bottomed flask which contained about 1.0 g of tin(II) *n*-butoxide (Sn(O*n*Bu)$_2$) as catalyst (0.1% by weight). The flask was then heated at 180-200°C (using heating mantle and vary AC scale 120) in an air condenser connected with short path distillation apparatus as shown in Figure 2.1. Heating and stirring were continued until the water ceased to distill from the reaction flask under atmosphere for about 3 hours. Then, heated at 120-130°C (using heating mantle and vary AC scale 80) before a gentle vacuum (about 4-5 mmHg) was applied to the system for 3 hours to facilitate further removal of water and to increase the polymer molecular weight. The product at this stage was low molecular weight PLLA.

Finally, for an additional period of about 3 hours, the reaction temperature was heated about 220-240°C (using heating mantle and vary AC scale 140) under reduced pressure of about 4-5 mmHg in order to thermally degrade the low molecular weight PLLA to yield L-lactide as a primary product. Crude L-lactide began to distill out of the flask to a receiving flask as light yellow, needle-like crystals. This crude product was obtained in approximately 99% yield. [61]
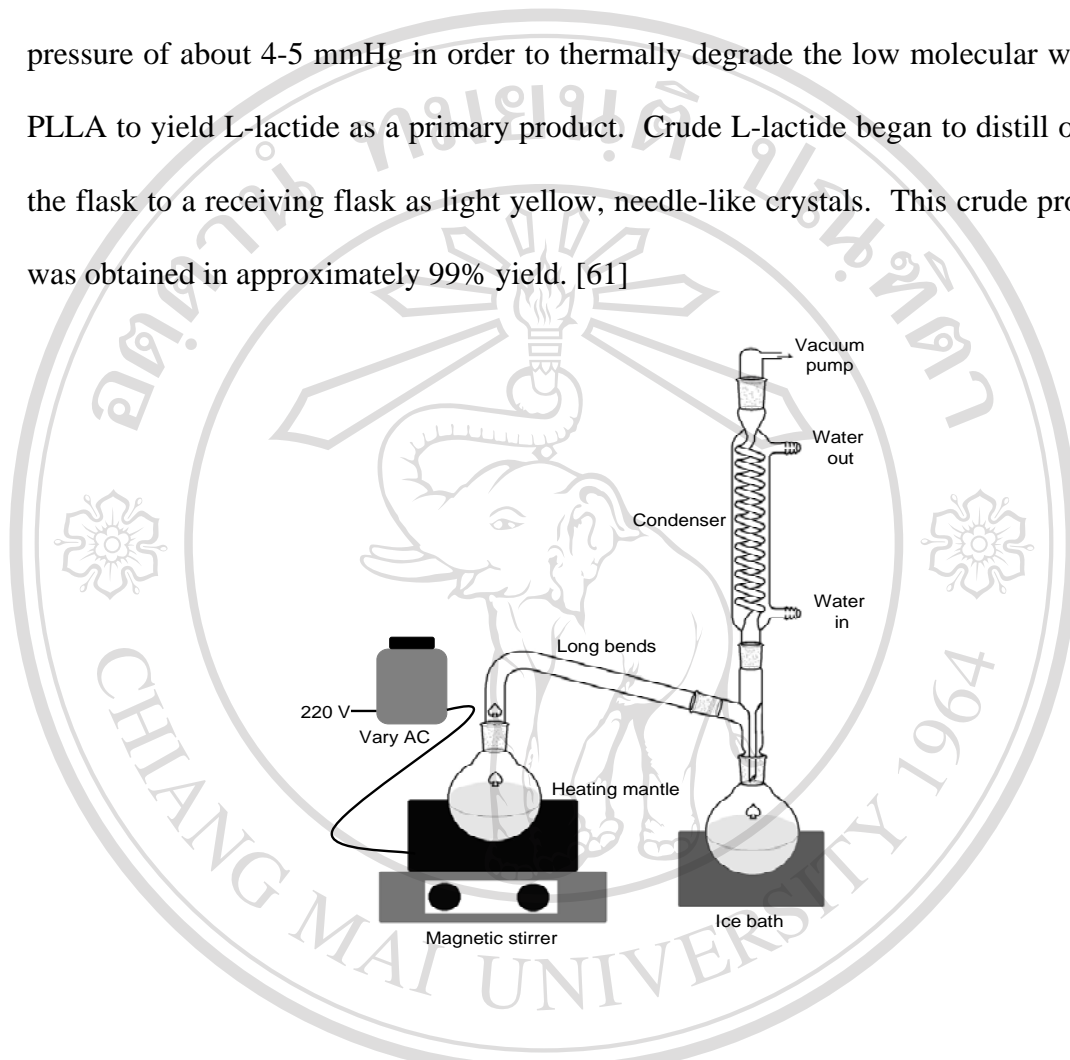

Figure 2.1 Apparatus used in the synthesis of L-lactide.

2.2.1.2 Synthesis and Purification of Tin(II) *n*-Butoxide

Tin(II) *n*-butoxide used as a catalyst in the synthesis of L-lactide, was synthesized using anhydrous tin(II) chloride, diethylamine and *n*-butyl alcohol in *n*-heptane *via* the reactions shown below:

$$SnCl_2 + 2(C_2H_5)_2NH \rightleftharpoons SnCl_2[NH(C_2H_5)_2]_2$$

$$SnCl_2[NH(C_2H_5)_2]_2 + 2ROH \rightleftharpoons Sn(OR)_2 + 2(C_2H_5)_2NH.HCl$$

For the synthesis of tin(II) *n*-butoxide, anhydrous $SnCl_2$ (3.79 g, 19.96 mmol) was dissolved in dried *n*-heptane (80 ml) under a nitrogen atmosphere. The mixture was cooled down to 10-20°C and diethylamine (5.2 ml, 49.91 mmol) was added. The reaction mixture was then left to stir at 10-20°C for 3 hours before *n*-butyl alcohol (4.24 ml, 79.86 mmol) was added and continued stirring at room temperature for a further 12 hours. The reaction mixture was filtered through a sintered glass filter and the solid product washed with *n*-heptane several times. The filtrate was evaporated to dryness, leaving behind 2.12 g (40% yield) of tin(II) *n*-butoxide as a pale brown viscous liquid which was stored under a nitrogen atmosphere. [62]

2.2.1.3 Purification and Purity Analysis of L-Lactide

The crude L-lactide was purified by recrystallisation three times from distilled ethyl acetate. The purified L-lactide was filtered through sintered glass porosity no.4 and washed with cold ethyl acetate. L-lactide crystalline solid was dried to constant weight at 55°C in a vacuum oven (about 3 mmHg). The purified L-lactide was obtained as a white needle-like crystalline solid. Purity analysis by differential scanning calorimeter (DSC) showed that the purified L-lactide had a sharp melting range 90-92°C as shown in Figure 2.2 and the melting peak temperature of L-lactide is 91.30°C.

In order to determine the actual purity of the recrystallized L-lactide by the DSC, the instrument's Purity Analysis Software Program was employed. [63] To

obtain the best results from purity analysis, a slow heating rate ($2°C$ min^{-1} or less) and

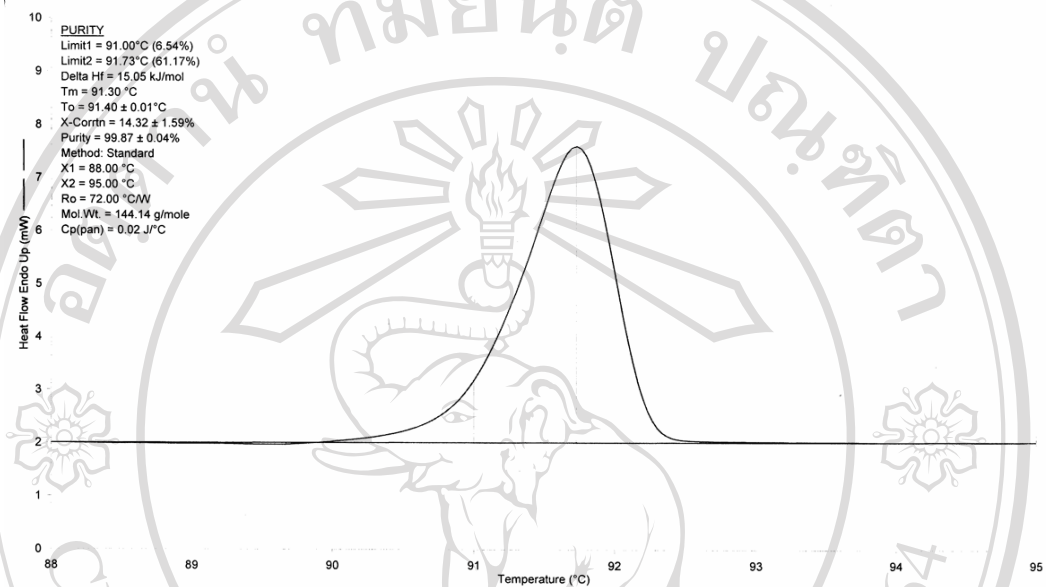a small sample size in the range of 1-3 mg are recommended.

Figure 2.2 DSC thermogram of purified L-lactide after three recrystallisations.
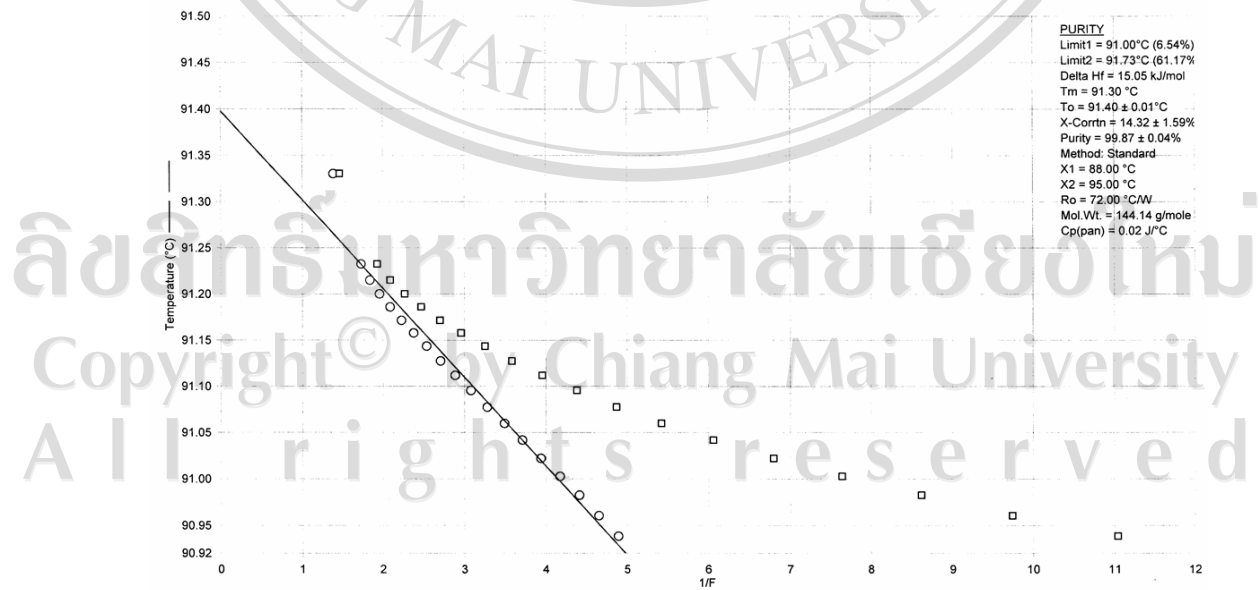

Figure 2.3 Van't Hoff plot of the purity analysis data for the purified L-lactide.

(F = mole fraction of sample which has melted)

From the Van't Hoff equation, a plot of the sample temperature (T_s) versus the reciprocal of the fraction of material melted at that temperature (1/F) gave a straight line with a negative slope equal in the magnitude to the melting point depression and an intercept on the Y axis (at 1/F = 0) is T_0.

$$T_s \quad = \quad T_0 - \frac{RT_0^2 X_2}{\Delta H_f} \times \frac{1}{F}$$

$$\text{Slope} \quad = \quad -\frac{RT_0^2 X_2}{\Delta H_f}$$

and   Intercept (at 1/F = 0)   = T_0

From its DSC melting curve and its Van't Hoff plot shown in Figures 2.2 and 2.3 respectively, a purity of 99.87% was obtained. These results served to show that the L-lactide synthesized in this work was of a sufficiently high purity (> 99.5%) to be able to produce high molecular weight polymers.

2.2.1.4 Structural Analyses of L-Lactide by FT-IR and ^{1}H-NMR Spectroscopy

The FT-IR spectrum of the L-lactide that was used in this work is shown in Figure 2.4 and could be compared with the reference spectra in Figure 2.5. The major vibrational peaks are listed in Table 2.3.

The ^{1}H-NMR and ^{13}C-NMR spectra of the L-lactide that was used in this work are shown in Figures 2.6 and 2.7 and could be compared with the reference spectrum in Figure 2.8. Both spectra were obtained from sample solutions in deuterated chloroform, CDCl$_3$, as solvent. The chemical shifts of the various peaks in the spectra are listed in Table 2.4 and the peaks assigned to the corresponding protons and

carbons.
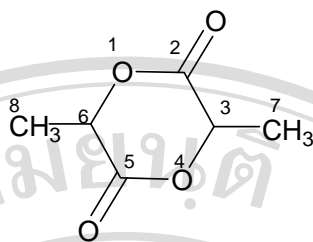
Scheme 2.1 Chemical structure of L-lactide.

Table 2.3 Main vibrational assignments in the L-lactide infrared spectra.

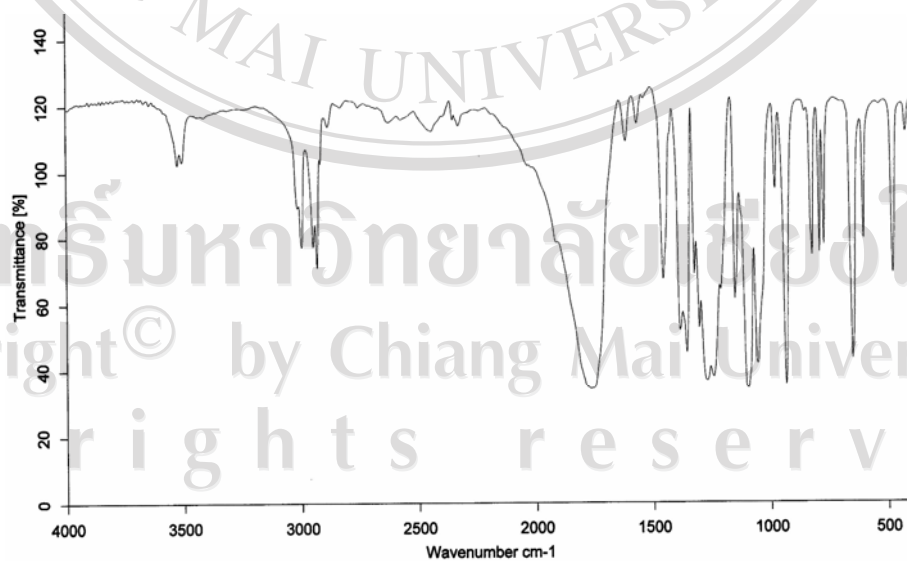| Wavenumber (ν, cm^{-1})	Vibrational assignment
2945-2935	C-H stretching of CH_2, CH_3
1780-1740	C=O stretching
1450-1380	C-H bending of CH_2, CH_3
1280-1240	C-O stretching in acyl-oxygen
1100-1080	C-O stretching in alkyl-oxygen

Figure 2.4 FT-IR spectrum of the L-lactide used in this work.

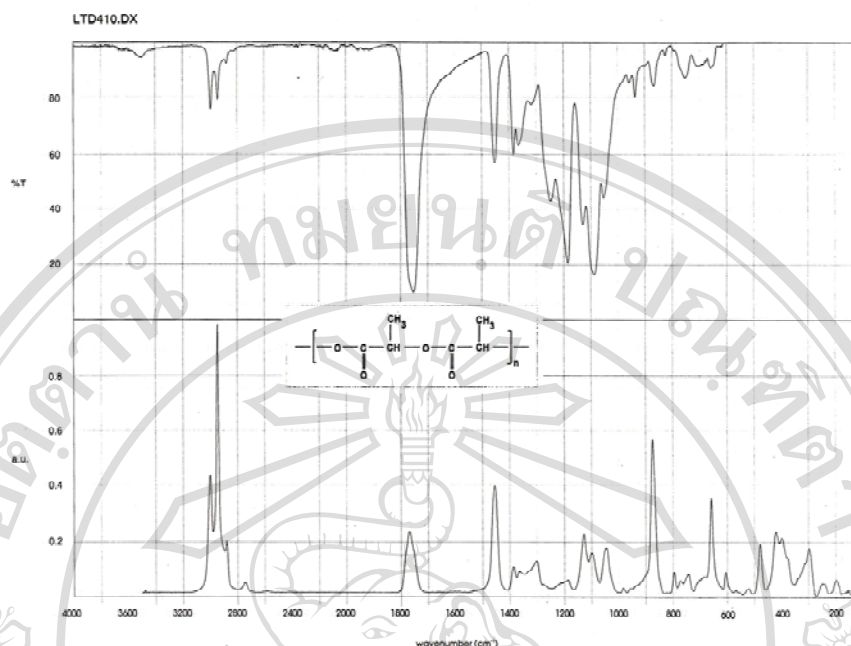**Figure 2.5** Reference FT-IR and FT-Raman spectra of the L-lactide. [64]

Table 2.4 ^{1}H-NMR and ^{13}C-NMR chemical shifts and proton assignments

for L-lactide.

^{1}H-NMR (400 MHz) in CDCl$_3$ solvent	
Chemical Shift (δ, ppm)	**Proton Assignment**
5.07	q , (J = 6.7 Hz), 2H , CH- 3,6
1.67	d , (J = 6.73 Hz), 6H , CH$_3$-7,8
^{13}C-NMR (100 MHz) in CDCl$_3$ solvent	
Chemical Shift (δ, ppm)	
167.42 (Cq-2,5), 72.41 (CH-3,6), 15.70 (CH$_3$-7,8)	

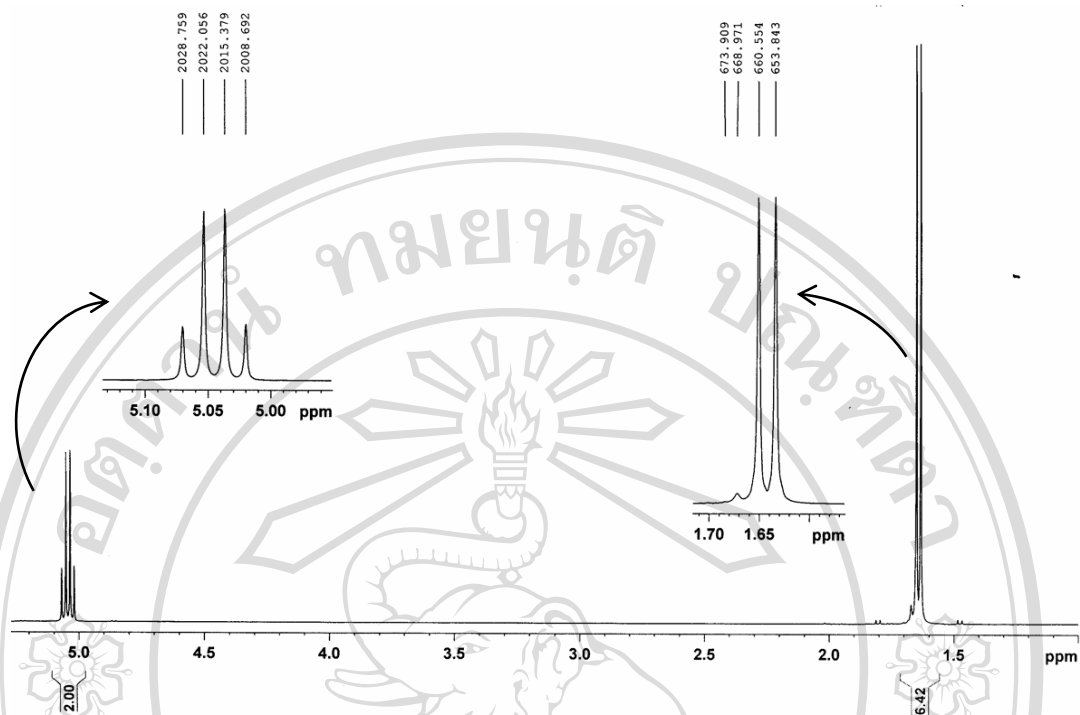**Figure 2.6** ^{1}H-NMR (400 MHz) spectrum of L-lactide used in this work in CDCl$_3$ as solvent at 25.0°C.
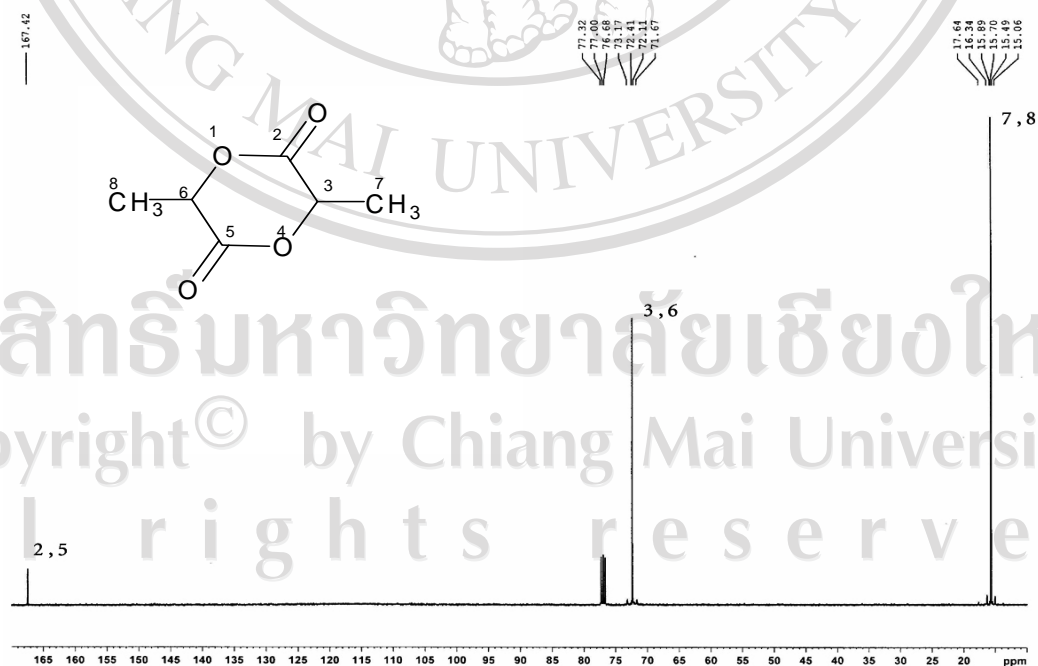

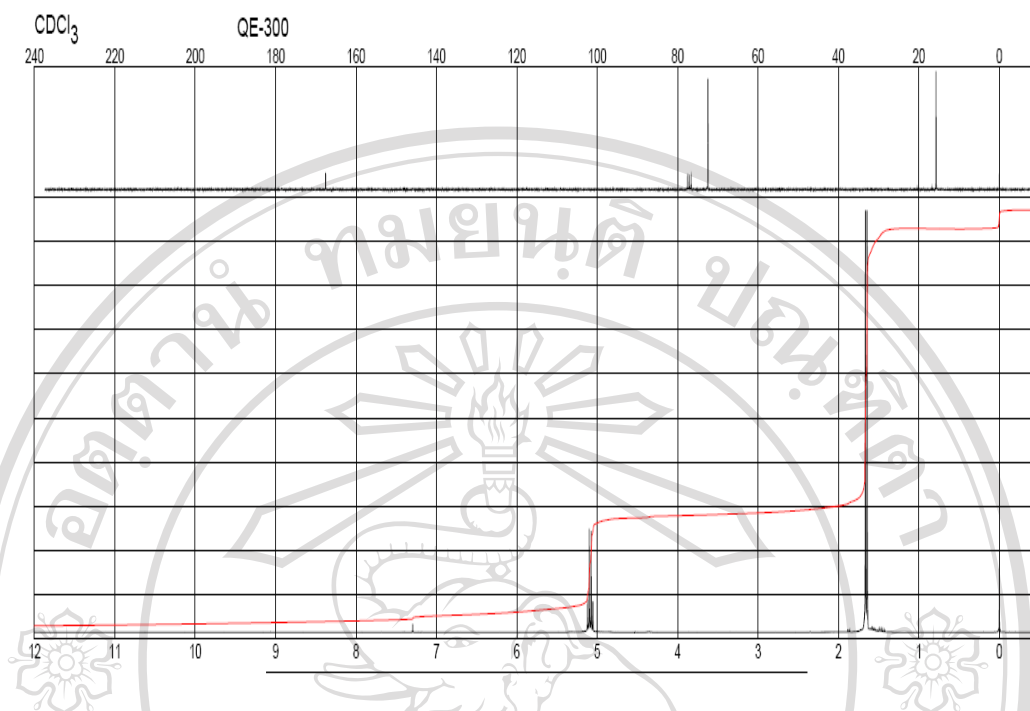**Figure 2.7** ^{13}C-NMR (100 MHz) spectrum of L-lactide used in this work in CDCl$_3$ as solvent at 25.0°C.

Figure 2.8 Reference ^{1}H-NMR (below) and ^{13}C-NMR (above) spectra of L-lactide.

[60]

2.2.1.5 Purification of ε-Caprolactone by Vacuum Distillation

Commercial ε-caprolactone (Acros) monomer was purified by vacuum distillation before used as shown in Figure 2.9. The constant boiling fraction from 72°C /0.8 torr (*cf.* ε-caprolactone boiling point = 80°C /0.75 torr [52]) being collected. Pure ε-caprolactone was obtained as a clear colorless liquid and was stored over molecular sieve 4 Å in a refrigerator in a tightly sealed container until required for use in polymerization.
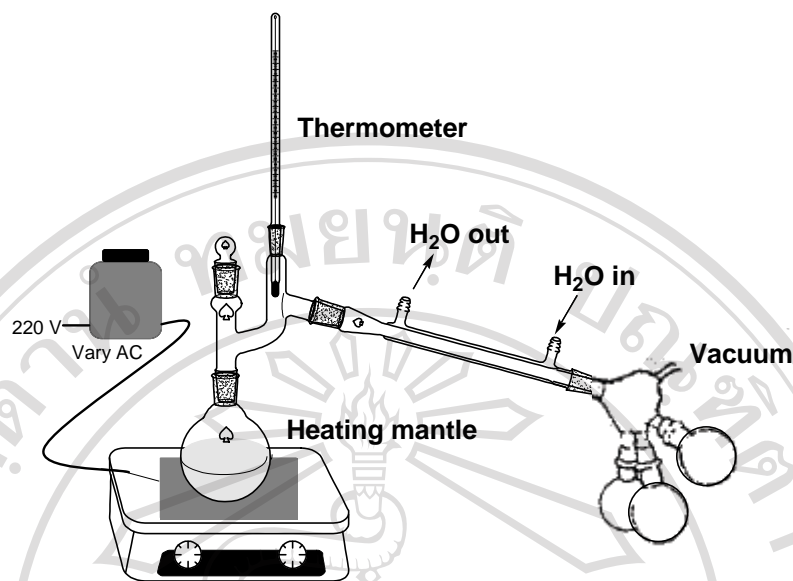
Figure 2.9 Vacuum distillation apparatus used for the purification of ε-caprolactone.

2.2.2 Catalyst and Initiator Purification

Because trace amounts of water and other impurities could be presence in the catalyst and various initiators used in this research project, they required further purification.

2.2.2.1 Stannous Octoate

Commercial stannous octoate, $SnOct_2$ (Sigma) typically 95% pure as received, commonly contains 2-ethyl hexanoic acid and water as impurities. $SnOct_2$ used in this research project was purified *via* 2 step distillations. The first step is the distillation at atmospheric pressure for removing residual water, and the second step is the distillation under vacuum at 120-126°C/15 torr for removing 2-ethyl hexanoic acid (*cf.* 2-ethyl hexanoic acid boiling point = 140°C/23 torr [65]). Purified $SnOct_2$ remaining in the heating flask was obtained as a pale yellow viscous liquid and was

stored in vacuum desiccators.

2.2.2.2 1-Hexanol

1-Hexanol (Merck), monofunctional hydroxyl initiator used for the preparation of linear polymers was purified by vacuum distillation. The distilled 1-hexanol was collected as the constant boiling fraction at 47°C/4.0 torr (*cf.* boiling point = 156°C/760 torr [65]) and was stored in vacuum desiccators.

2.3 Synthesis of poly(L-lactide-*co*-ε-caprolactone), PLC 50: 50 copolymers.

In this research, the influence of synthesis scale-up (25 g, 250 g and 500 g) on the % yield, copolymer composition, microstructure, thermal properties and molecular weight have been studied. All ROP of PLC 50:50 mole% copolymers were carried out in bulk in the round-bottomed flask for 25 g, flat-flange flask for 250 g and Parr reactor for 500 g as shown in Figures 2.10 (a-c), respectively. All glassware was dried in a vacuum oven at 100°C for 12 hours and cooled in a dry glove box before use.

The monomers (LL and CL), catalyst (Sn(Oct)$_2$) and initiator (1-hexanol) were weighed and added to the reaction flask under dry nitrogen in a controlled atmosphere glove box at room temperature. After removing the reaction flask from the glove box, the copolymerization was carried out at a constant temperature and for a given period of time. At the end of the polymerization period, the reaction flask was allowed to cool to room temperature. The polymer products were dissolved in chloroform

followed by re-precipitation in cold methanol as shown in Figure 2.11. Then, the copolymer products were dried in a vacuum oven at 60°C until constant weight.

(a)

(b)

(c)

Figure 2.10 Apparatus for ROP of PLC (a) small scale, 25 g (b) medium scale, 250 g

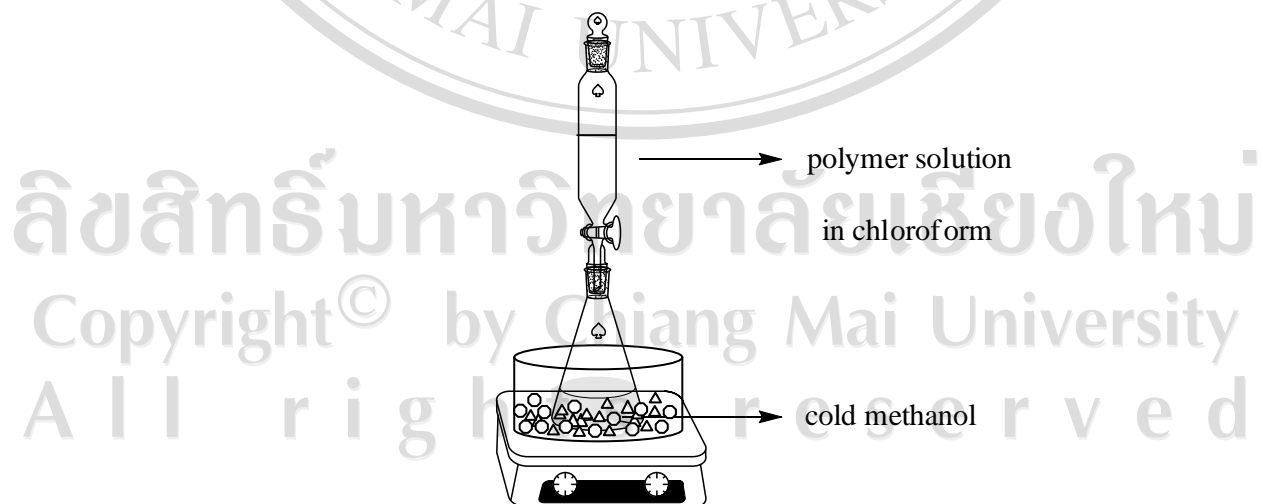(c) large scale (Parr Reactor Model 4520), 500 g.

polymer solution

in chloroform

cold methanol

Figure 2.11 Apparatus used for polymer re-precipitation.

2.3.1 Synthesis of Poly(L-lactide-*co*-ε-caprolactone), PLC 50:50

mole% Copolymers : Small Scale Synthesis (25 g)

The polymerizations were carried out in 50 ml round-bottomed flasks. A magnetic bar was enclosed in the reaction flask as shown in Figure 2.10 (a). The effects of reaction time (2, 4, 6, 8, 12, 24, 48, 72 and 96 hours), reaction temperature (110, 120, 130 and 140°C) and monomer to initiator molar ratio (100:0.002 to 100:0.20 by mole) on PLC 50:50 mole% copolymer properties were studied.

2.3.2 Synthesis of Poly(L-lactide-*co*-ε-caprolactone), PLC 50:50

mole% Copolymers : Medium Scale Synthesis (250 g)

The polymerizations were carried out in a 250 ml closed flat-flange flasks. A magnetic bar was enclosed in the reaction flask as shown in Figure 2.10 (b). The ROP was carried out in bulk at 120°C and using 0.1 mole% $SnOct_2$ as a catalyst and 0.01 mole% 1-hexanol as an initiator. The effect of reaction time on PLC 50:50 mole% copolymer properties were studied. The reaction time was varied from 2 to 121 hours (2, 3, 4, 6, 8, 11, 24, 48, 72, 96 and 121 hours).

2.3.3 Synthesis of Poly(L-lactide-*co*-ε-caprolactone), PLC 50:50

mole% Copolymers : Large Scale Synthesis (500 g)

The polymerizations were carried out in a Parr Reactor Model 4520 as shown in Figure 2.10 (c). The effect of reaction time on PLC 50:50 mole% copolymer properties were studied.

The Parr Reactor Model 4520 consists of 2 parts: Bench top reactors and temperature controllers were shown in Figure 2.12 (a) and (b).
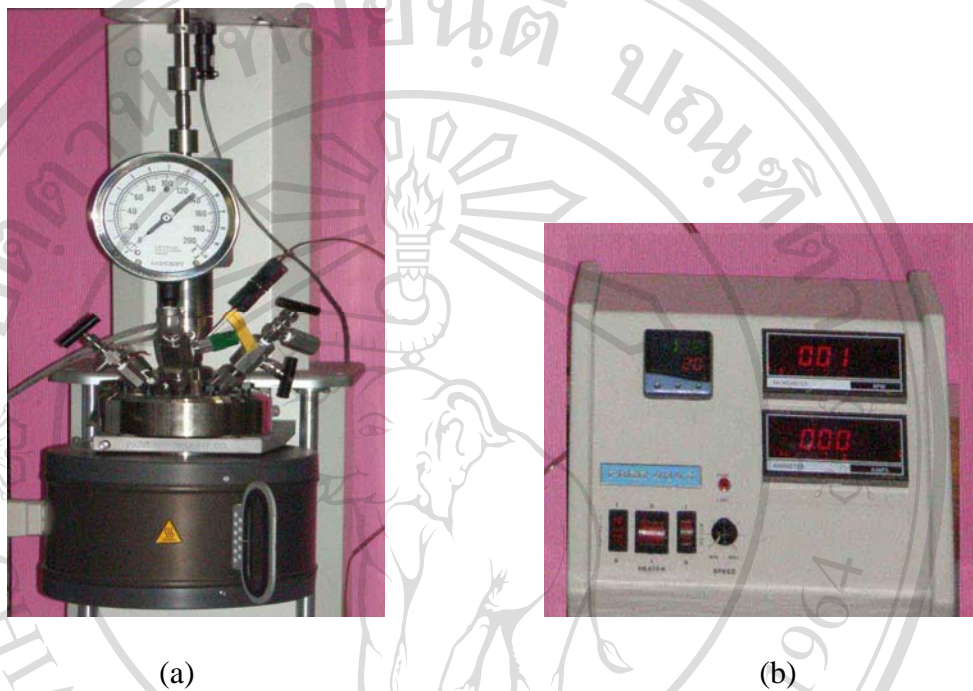

(a)   (b)

Figure 2.12 Parr Reactor Model 4520 (a) Bench top reactors (b) temperature

controllers.

2.4 Characterization Methods

In this research project, the monomers, initiators, catalysts and polymer products obtained were characterized by the following combination of instrument methods.

2.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy (FT-IR) is the most extensively used method for the analysis of functional groups. In this research project, FT-IR was

used, mainly for the structural characterization of the catalyst. A Bruker FTIR TENSOR 27 Fourier Transform Infrared Spectrometer was used for the recording of FT-IR spectra with the range $400 - 4000$ cm^{-1}. The samples were prepared in the form of neat liquid on a sodium chloride plate.

2.4.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

Polymer structures, compositions and monomer sequencing were characterized by a combination of 400 MHz ^{1}H and 100 MHz ^{13}C nuclear magnetic resonance (NMR) spectroscopy using a Bruker Avace spectrometer. The samples were dissolved in deuterated chloroform (CDCl$_3$) at a concentration of 6% (w/v) for ^{1}H-NMR and 12% (w/v) for ^{13}C-NMR. The spectra were obtained from MestRe-C data processing software.

2.4.3 Gel Permeation Chromatography (GPC)

Molecular weight ($\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_v$) and polydispersities ($\overline{M}_w / \overline{M}_n$) of the polymers were determined by gel permeation chromatography (GPC). The Waters Associated system equipped with a Waters 717 plus Autosampler injector, a Waters 515 HPLC solvent pump with styragel HR4E&5E column (pore size; 5 μm) connected a Waters 2414 Refractive Index and Viscotek 270 Dual detectors at 40°C and a TriSEC Version 3.00 as data processing software was used. Narrow polydispersities polystyrene standards were used for calibration, range 2,950-1,270,000 g mole^{-1}. Tetrahydrofuran (THF) was used as the eluent and was delivered at the flow rate of 1.0 ml min^{-1}. The samples were dissolved in THF at a

concentration of 3-5% (w/v).

2.4.4 Dilute-Solution Viscometry

The intrinsic viscosities were determined from dilute solution viscometry. The viscosities were measured at concentration of 0.2-1.0% (w/v) in chloroform at 25°C with Schott-Gerate Ubbelohde type viscometer (type No. 532 00, capillary No. 0_c) in conjunction with Schott-Gerate AVS300 Automatic Viscosity Measuring System. Each solution concentration was separately prepared in order to eliminate any dilution errors. The solutions were filtered and allowed to thermally equilibrate at the water bath temperature (25.0±0.1°C) before measurement. The results were plotted between reduced and inherent viscosity versus concentration. The double extrapolation to a common point facilitates the accurate estimation of the intrinsic viscosity.

2.4.5 Differential Scanning Calorimetry (DSC)

The purities, temperature transitions (T_g, T_c and T_m) and morphology (% crystallinity) were investigated by differential scanning calorimetry (DSC). DSC measurement was made on a Perkin-Elmer DSC7 instrument with Pyris software. Pure indium and tin were used as a reference material to calibrate the temperature. The thermal properties measurements were run from -20°C to 200°C at a heating rate of 10°C min^{-1}. The samples with a typical mass of 3-5 mg were encapsulated in sealed aluminum pans and were heated and cooled under nitrogen atmosphere.

In order to determine the actual purity of the monomers by the DSC, the

instrument's Purity Analysis Software Program was employed. The measurements were run at a slow heating rate of 2°C min^{-1} and small sample sizes in the range of 1–3 mg are recommended.

2.4.6 Thermogravimetric Analysis (TGA)

Thermogravimetry (TG) was used as a method for the investigation of the thermal stability and decomposition profile of a polymer. TG analysis was carried out on a Perkin-Elmer Pyris instrument with a TGA7 model. The heating rate used was 20°C min^{-1} and the sample was heat from 50°C to 600°C with initial sample weights in the range of 5-10 mg. Data was recorded as a thermogram of % weight versus temperature.

2.4.7 Mechanical (Tensile) Testing

The mechanical tests performed on Lloyds LRX+ Universal Mechanical Testing Machine as shown in Figure 2.13 were used for determining the mechanical properties such as tensile strength, %elongation at break and Young's modulus. The polymer films were prepared by solvent casting method using chloroform as solvent (2.4 g/30 ml) in mold (12x15 cm^2) and then the solvent allowed to evaporate slowly in air at room temperature for 48 hours. The obtained films were further dried under vacuum at room temperature for 48 hours. The films were cut with wide 10 mm, length 100 mm. The test conditions were followed as ASTM D882-91 with a sample grips, gauge length 50 mm, load cell of 0.1 N (preload = 0.1 N) at a crosshead speed of 500 mm min^{-1}. The tests were required at least five samples from each polymer at
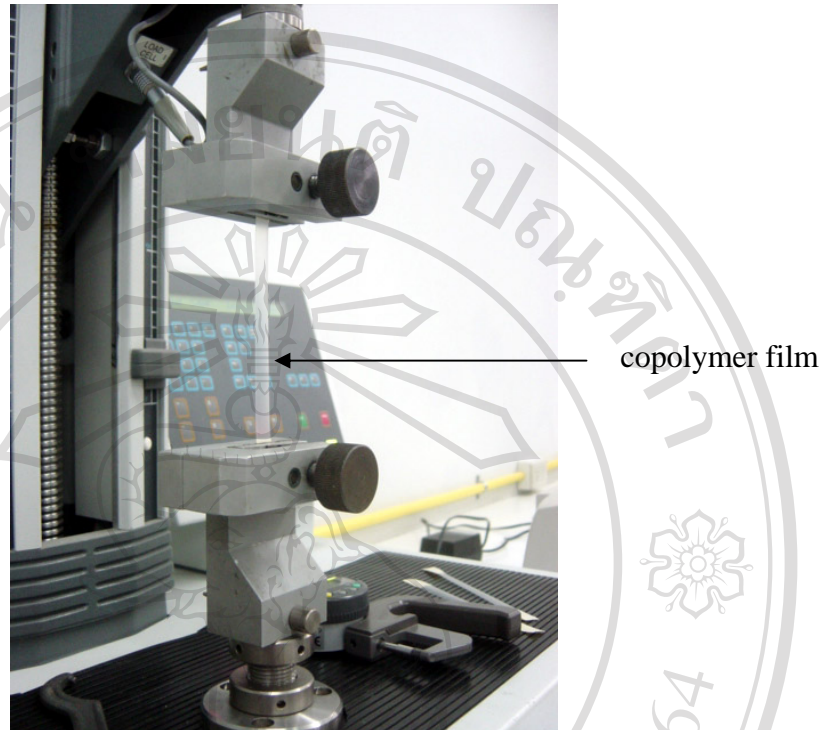
25±2°C and 50±5 % relative humidity. [66]

copolymer film

Figure 2.13 Lloyds LRX + Universal Mechanical Testing Machine.

2.4.8 Dynamic Mechanical Analysis (DMA) [67]

Dynamic mechanical analysis (DMA) is a particular kind of relaxation spectroscopy in which the sample is perturbed by a sinusoidal force and the response of the material is measured over a range of temperatures and at different frequencies of the applied force. From an analysis of the material response it is possible to derive information about the molecular motions in the polymer and how these affect the modulus, damping characteristics and structural transitions.

A variety of deformations could be applied, including shear, bending, tension and torsion. The choice of deformation was required. For instance, the tension mode is more appropriate for fiber and thin films, the bending mode for composite materials

and the shear mode for elastic materials.

The dynamic mechanical properties of the materials in the shear mode are described in term of the complex dynamic modulus, E* :

$$E* = E' + iE''$$

where   E*   =   the complex dynamic modulus

             E'   =   the storage (elastic) modulus and

             E''   =   the loss modulus

also $\tan \delta$ =   E''/E'   where δ is the phase angle lag.

It is important to note that beta and gamma transitions are too faint to be detected in the different scanning calorimeter (DSC). The DMA is much more sensitive than DSC technique and can easily measure transitions not apparent in other thermal methods. This sensitivity allows the DMA to detect the glass transition temperature (T_g) of PLC copolymer in this study.

Dynamic mechanical properties of polymers were investigated in the solid state below the respective melt temperatures, using a Dynamic Mechanical Analyzer (Mettler Toledo DMA/SDTA 861[e]) as shown in Figure 2.14. Storage modulus (E'), loss modulus (E'') and damping (tan δ) were measured using the film in shear mode, in the temperature range approximately -100°C to 150°C, the rate of heating was with 4°C min^{-1} and applied at a frequency of 1 Hz in air, maximum force 3 N and maximum displacement amplitude 20 μm. Liquid nitrogen was used as the furnace coolant. The film specimens were prepared by solvent casting method using chloroform as solvent as described in section 2.4.7. The films were cut in diameter of wide 4.85 mm, length 5.37 mm and thickness 0.65 mm.

Figure 2.14 Mettler Toledo DMA/SDTA 861ᵉ apparatus.

2.4.9 Melt Rheology Measurements [68-69]

Rheology is defined as the science of the deformation and flow of mater. All polymers melts are viscoelastic materials; that is, their response to external load lies in varying extent between that of a viscous liquid and an elastic solid. In an ideal viscous liquid, the energy of deformation is dissipated in the form of heat and cannot be recovered just by releasing the external forces; whereas, in an ideal solid, the deformation is fully recovered when the stresses are released. Due to the dependence of rheology on the structure and the basic inherent chemistry of the polymers, rheological data can be used effectively to control material parameters like molecular weight, molecular weight distribution, branching, crosslinking and so forth so that the right choice of the polymer to be processed can be made under a given set of processing conditions. Viscosity is a measure of a fluid's resistance to flow and describes the internal friction of a moving fluid. Viscosity is an extremely important

property of polymer melts and solutions since it controls the possibility of processing. If the viscosity is too high, processing will be difficult or impossible.

Rheological measurements were made using oscillating rheometers in order to obtain the complex shear modulus, $G^*(\omega)$ as a function of frequency and/or temperature. The response of the sample yields the shear storage modulus (G′), which indicates the elastic character of the material, and the shear loss modulus (G″), which related to viscous response of the materials.

Figure 2.15 Bohlin Gemini HR^{nano} Rotational Rheometer apparatus.

(a) parallel plate geometry   (b) the gap between the plates

Measurements on PLC copolymer were performed using Bohlin Gemini HR^{nano} Rotational Rheometer, Malvern as shown in Figure 2.15. The diameter of the

plates was 25 mm and the gap between the plates was set to 0.5 mm. The PLC copolymer was placed between the plates and heated to the test temperature (150°C) in order to eliminate previous deformation and thermal history. All measurements were made in the linear viscoelasticity region, which ensured by a dynamic strain frequency sweep. Rheological characterization was performed under nitrogen at 130, 140 and 150°C. Samples were analyzed in a parallel plate geometry by using a dynamic strain of 5% applied the frequency from 0.01 to 100 Hz (0.0628 to 628 rad/s). The technique employs a dynamic frequency sweep under isothermal conditions to study time-temperature superposition of polymer. The moduli G′ and G″ were thus monitored as a function of frequency.

2.4.10 Fabrication of Small Tubes by Dip-Coating

The PLC copolymer was dissolved in distilled chloroform (15%w/w) and Kirchner (K) wires with a diameter of 1.20 mm used as moulds. K wires was immersed to a depth of 5 cm in a copolymer solution at a speed of 9 mm/sec (scale 30) and held for 30 seconds as shown in Figure 2.16 (a). It was then pulled out at the same speed and rotated at 30 rpm for 15 min to allow the solvent to evaporate as shown in Figure 2.16 (b). The procedure was then repeated two times to increase the tube thickness. The K wires were stored in desiccators under vacuum for 3 days and dried in a vacuum oven at room temperature until constant weight in order to complete drying. The copolymer tubes on the K wire was then frozen in cold anhydrous methanol before stripping off and were stored in desiccators under vacuum. For dip-coating method, the thickness of nerve guide tubes depends on the concentration of the copolymer solution and the dipping-times. The inner diameter of

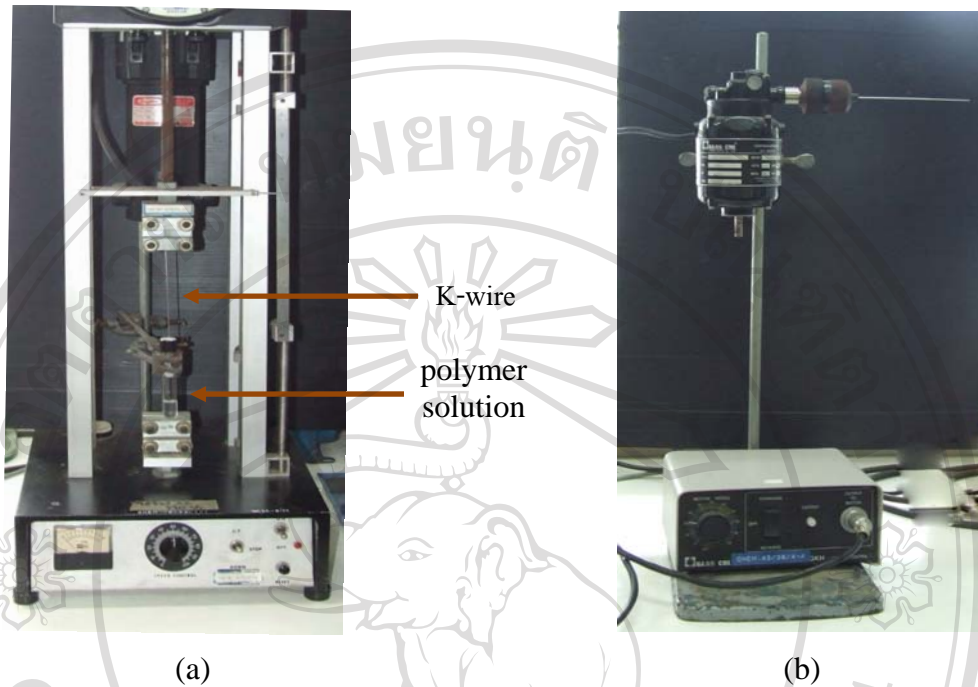nerve guide tubes depends on the diameters of K wires.

(a)   (b)

Figure 2.16 Dip-Coating Apparatus.

(a) K wire immersed to copolymer solution

(b) Rotate K wire in horizontal line to evaporate solvent

2.4.11 Fabrication of Small Tubes by Melt Extrusion

From dip-coating method as described in section 2.4.10, it is easily method and rather laborious. The small tubes could uniform and controllable dimensions. Nevertheless, it is time-consuming method and the length of tubes has limit from the length of moulds. Thus, melt extrusion method was also used to prepare small tubes of similar dimensions, longer tubes and without solvent.

For the fabrication of small tubes by melt extrusion, the polymer is heated above its melting temperature (T_m) but below degradation temperature (T_d). The polymer is displaced downward through the melting zone towards a tubular-shaped

die by applying pressure to a ram that acts as a piston applied to the top of the unmelted polymer in the well. The polymer is first converted into a rod that fits into the well by a melting process. The molten polymer emerging from each orifice in the tubular-shaped die is guided to a cooling zone where the polymer solidifies to complete the tubes formation process.

In this study, melt extrusion method were used in the production of small tubes of PLC copolymer using small-scale melt spinning apparatus manufactured by Ventures&Consultancy Bradford Ltd., UK as shown in Figure 2.17. The various accessories used in the small-scale melt spinning apparatus as shown in Figures 2.18-2.20. It could handle batch sizes of as small as 5-20 g depending on the size of the cylinder that was used. The melt extrusion method consists of 2 steps as follow:

Step 1 is the pre-formed rod preparation. The polymer samples, cut up into small pieces, were first heated and then compressed into pre-formed cylindrical rods. Figure 2.18 showed the accessories used in the pre-formed rod preparation, the cylinder assembly was placed in the extrusion unit, the heater plug connected and the thermocouple inserted into its hole. The polymer was then compressed with a ram speed of 5 mm/min while being heated up to the required rod preparation at temperature of 140°C. The temperature was then held constant for 15 min so that homogenous polymer chips melted in the shape of a cylindrical rod without air bubble. The polymer rod was cooled and removed from the cylinder and then stored in vacuum desiccators until required for used in fabrication of small tubes.

Step 2 is fabrication of small tubes from pre-formed rod using small-scale melt spinning apparatus. A closer view of the various accessories used is shown in the photograph in Figures 2.19-2.20. A more detailed diagram of the internal

compression, melting and metering zones is shown in Figure 2.21. A pre-formed polymer rod was carefully inserted into the extrusion cylinder and the ram (piston) placed in position. The extrusion cylinder was placed in the extrusion unit with the thermocouple and band heater in place. The polymer rod was then compressed until the ram could no longer more, the ram control switched off and the rod heated up to the temperature of 135°C. When this temperature had been reached and equilibrated for 15 min, the ram control was switched on again and extrudes the molten polymer with a ram speed of 2 mm/min. As the extruded tube emerged from the tubular-shaped die and cooled in water cooling bath (~10-15°C). Finally, the small tubes were collected in vacuum desiccators.
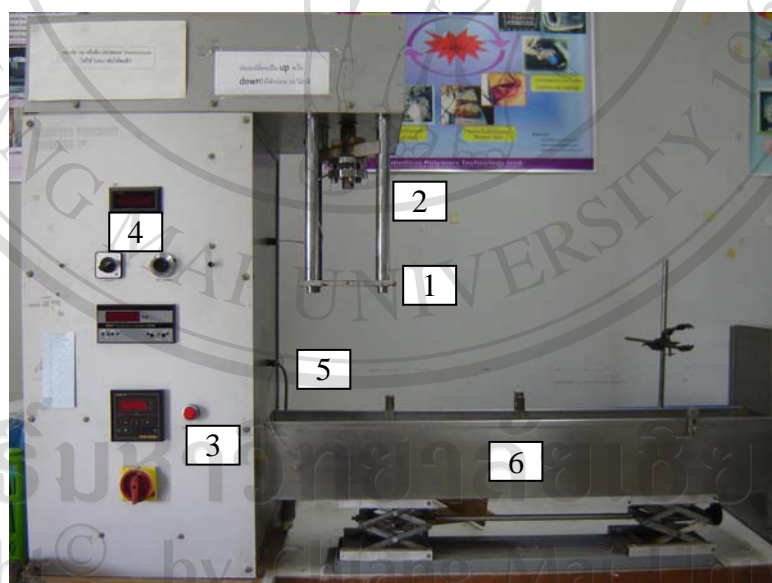

Figure 2.17 Photograph of the small-scale melt spinning apparatus.

    (1) extrusion cylinder block   (2) piston (ram)

    (3) heater control button   (4) ram speed control switch

    (5) thermocouple   (6) cooling water bath

Figure 2.18 The various accessories used in pre-formed polymer rod preparation.

Figure 2.19 The various accessories used in the fabrication small tubes by

melt extrusion.

5 cm

Figure 2.20 The tubular-shaped die in the fabrication small tubes by
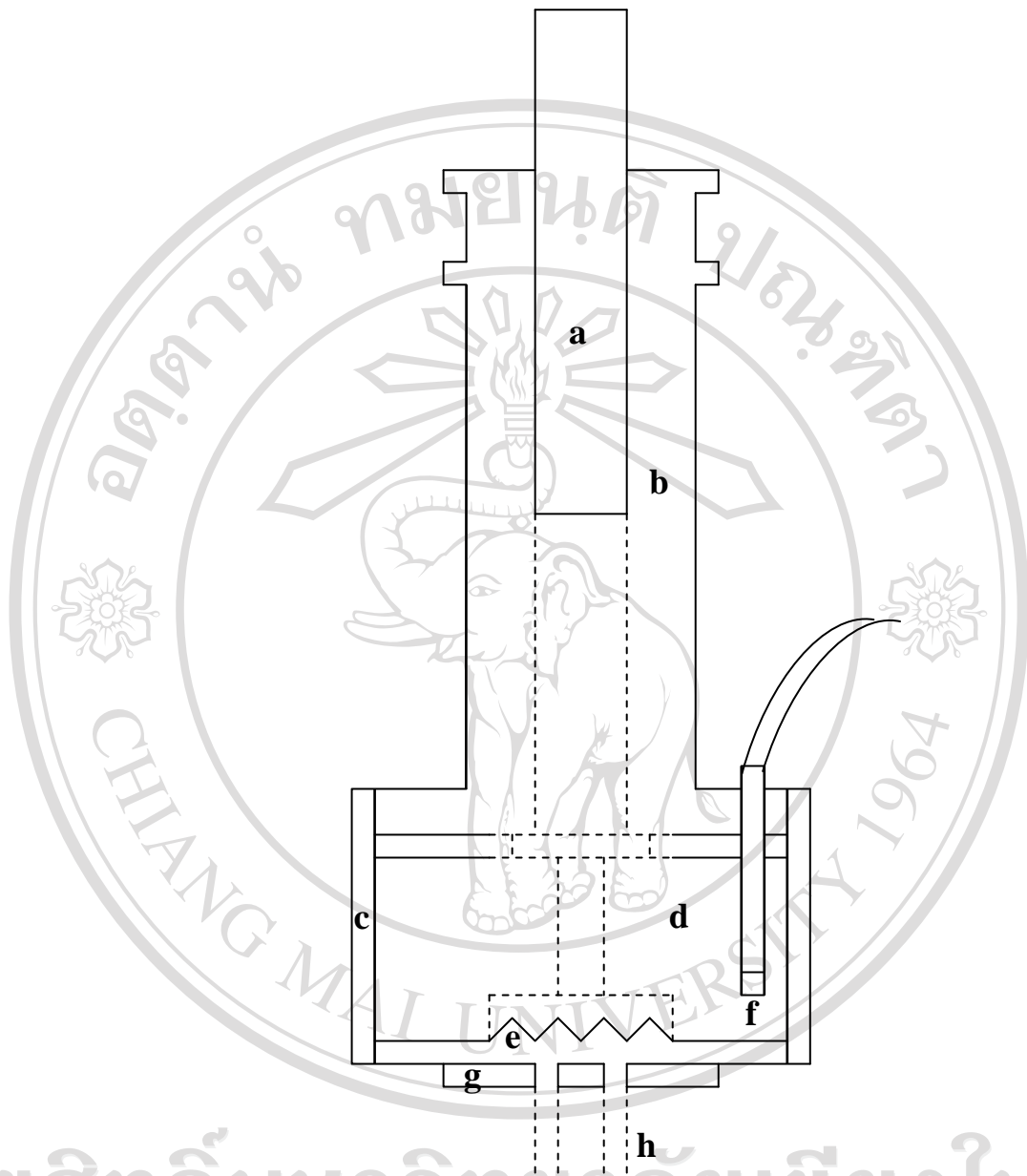
melt extrusion.

Figure 2.21 Schematic diagram of the compression, melting and metering zones

showing the (a) ram, (b) cylinder, (c) band heater, (d) heating block,

(e) stainless steel filter mesh, (f) thermocouple, (g) tubular-shaped die

and (h) extruded tubes.