CHAPTER 2

EXPERIMENTAL

2.1 Chemicals, Apparatus and Instruments

2.1.1 Chemicals

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

Table 2.1 Chemicals used in this research project.

CHEMICAL	USAGE	GRADE	SUPPLIER
ε-Caprolactone	Monomer	Purum, GC	Fluka
L(+)-Lactic acid	Monomer precursor	88%	Carlo Erba
Stannous octoate *	Catalyst	95%	Sigma
1-Hexanol	Initiator	GC	Merck
1,3-Dimethyl-2,2-propanediol	Initiator	Purum, GC	Fluka
1,1,1-Tris(hydroxymethyl) propane	Initiator	Purum, GC	Fluka
Pentaerythritol	Initiator	Purum, HPLC	Fluka
Antimony trioxide	Catalyst	99%	BDH
p-Toluene sulfonic acid	Catalyst	AR	Merck
Chloroform	Solvent	AR	Lab Scan
Ethyl acetate	Solvent	Commercial	ICI
Toluene	Solvent	Commercial	ICI
Tetrahydrofuran	Solvent	HPLC	Carlo Erba

Table 2.1 (continued)

CHEMICAL	USAGE	GRADE	SUPPLIER
n-Hexane	Non-solvent	Commercial	ICI
Acetone	Solvent	Commercial	ICI
Calcium chloride	Drying agent	AR	Carlo Erba
Calcium hydride	Drying agent	AR	Carlo Erba
Molecular sieves 4 Å	Drying agent	Commercial	Aldrich
Silicone oil	Heating bath	Commercial	Fluka

* systematic name = Tin(II)-bis-2-ethylhexanoate

2.1.2 Apparatus and Instruments

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

Table 2.2 Apparatus and Instruments used in this research project.

APPARATUS AND INSTRUMENTS	COMPANY	MODEL
FT-IR Spectrometer	Nicolet	510
NMR Spectrometer	Bruker	Avance
Thermogravimetric Analyzer	Perkin-Elmer	TGA7
GC-MS Spectrometer	Agilent Technologies	GC6890
	Hewlett Packard	MSD5973
Differential Scanning Calorimeter	Perkin-Elmer	DSC7
Gel Permeation Chromatograph	Waters	150-CV
Automatic Viscosity Measuring System	Schott-Gerate	AVS300
Universal Mechanical Testing Machine	Lloyd Instruments	LRX+
Controlled Atmosphere Glove Box	Labconco	50004
Vacuum Oven	Eyela	VOS-301SD
Rotary Evaporator	Buchi	R-200

2.2 Characterization Methods

In this research project, the monomer, initiators, catalyst and polymer products obtained were characterized by the following combination of instrumental methods.

2.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectroscopy 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 Nicolet FT-IR 510 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.

2.2.2 Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR and ^{13}C-NMR)

Nuclear magnetic resonance (NMR) spectroscopy was used to analyze the chemical composition, number-average molecular weight and microstructure of the polymer formed in this research project. For NMR measurement, the samples were dissolved in deutero-chloroform in 5 mm NMR tubes at 30°C. The sample concentration was about 5% by weight. Chemical shifts were relative to tetramethylsilane (internal standard at $\delta = 0$ ppm). Both ^{1}H-NMR and ^{13}C-NMR spectra were obtained from MestRe-C data processing software and recorded on a Bruker Avance spectrometer working at 400 MHz and 100 MHz respectively.

2.2.3 Thermogravimetry (TG)

Thermogravimetry (TG) is a most useful 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. Nitrogen gas was used as the purge gas at pressure of 30 lbs in^{-2} for the sample zone and 50 lbs in^{-2} for the balance zone. 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.

2.2.4 Gas Chromatography–Mass Spectroscopy (GC-MS)

In this research project, gas chromatography–mass spectroscopy (GC-MS) was used for the structural identification of catalyst. The samples were analyzed utilizing an Agilent GC 6890 gas chromatography–Hewlett Packard MSD 5973 mass spectrometer. The GC was equipped with a HP 19091S-433 capillary column (30 m x 0.25 mm id. x 0.25 μm film thickness). Helium was used as carrier gas. The samples were analyzed utilizing the following temperature program of the column: the temperature was allowed to rise from 100°C to 250°C at a heating rate of 10°C min^{-1} and then held at 250°C for 25 minutes. The Agilent 7683 series injector maintained a temperature of 250°C at split ratio of 20:1.

2.2.5 Differential Scanning Calorimetry (DSC)

The purities and thermal properties of monomer, initiators and synthesized polymers were investigated by differential scanning calorimetry (DSC). A number of important physical changes in a polymer may be measured by DSC, including the glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m). DSC measurement was made on a Perkin-Elmer Pyris instrument with a DSC7 model. Pure indium and tin were used as a reference material to calibrate the temperature scale and the heat capacity was calibrated by the pure indium before the sample was tested. The thermal properties measurements were run from -25°C to 120°C for low molecular weight polymers and from 0°C to 150°C for high molecular weight polymers at a heating rate of 10°C min^{-1}. The samples with a typical mass of 3-5 mg were encapsulated in sealed aluminium 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.

2.2.6 Gel Permeation Chromatography (GPC)

Molecular weight (MW) and molecular weight distribution (MWD) of the polymers were determined by gel permeation chromatrography (GPC). The Waters Associates system equipped with a Waters 717 plus Autosampler injector, a Waters 515 HPLC solvent pump with styragel HR4E&5E columns (pore size: 5 μm) connected a Waters 2414 Refractive Index and Viscotek 270 Dual detectors and a TriSEC Version 3.00 as data processing software was used. Narrow MWD polystyrene standards were used for calibration, range 1,100-186,000 g mole^{-1}. Tetrahydrofuran was used as an eluent and was delivered at a flow rate of 1.0 ml min^{-1} and the injection volume was 100 μl at 40°C. The samples were dissolved in Tetrahydrofuran at a concentration of 3-5% (w/v).

2.2.7 Dilute-Solution Viscometry

Measurements of diluted-solution viscosity were used for determining molecular weight. The viscosities were measured at concentrations of 0.1-0.8% (w/v) in chloroform at 30°C with a Schott-Gerate Ubbelohde type viscometer (type No. 532 00, capillary No. 0c) in conjunction with the 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 bath temperature (30°C) before measurement. The results were plotted between reduced and inherent viscosity versus concentration and the viscosity-average molecular weight were calculated from intrinsic viscosity and constants as the Mark-Houwink Sakurada Equation.

2.2.8 Mechanical Testing (Tensile Testing)

The mechanical tests performed on Lloyds LRX+ Universal Mechanical Testing Machine were used for determining the mechanical properties such as tensile strength, % elongation at break, and Young's modulus. Thin sheeting film samples were prepared by a simple solvent casting method. The polymer was dissolved in ethyl acetate to form solutions with concentrations of 20% (w/v). The solution was spread over a glass container (10 cm x

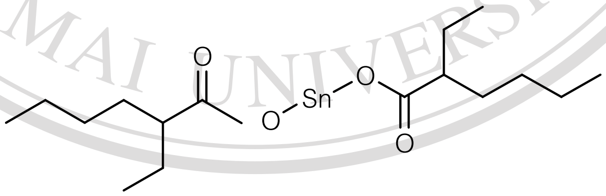
15 cm). The solvent was evaporated slowly in air at room temperature over three days. Each film was cut into 1.0 cm widths and 15.0 cm lengths and kept in a vacuum desiccator until use. The test conditions were followed as ASTM D882-91 with a sample grips, load cell of 100 N (preload = 0.1 N) at a crosshead speed of 10 mm min^{-1}. The tests were required at least five samples from each polymer at $23\pm2^{\circ}$C and 50 ± 5% relative humidity.

2.3 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. Since moisture (especially) can have a serious effect on the polymer molecular weight obtained.

In general, the method used was followed from references with appropriate drying agent employed.

2.3.1 Stannous Octoate



Stannous Octoate; $SnOct_2$
(Tin(II)-bis-2-ethylhexanoate)

2.3.1.1 Purification by Fractional Distillation

Commercial stannous octoate, $SnOct_2$, typically 95% pure as received, commonly contains 2-ethyl hexanoic acid and water as impurities. The acid is known to be very difficult to remove, even by careful fractional distillation under vacuum (Figure 2.1).

However $SnOct_2$ 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 [88] boiling point = 140°C/23 torr). Purified $SnOct_2$ remaining in the heating flask was obtained as a pale yellow viscous liquid and was stored over molecular sieves 4 Å.

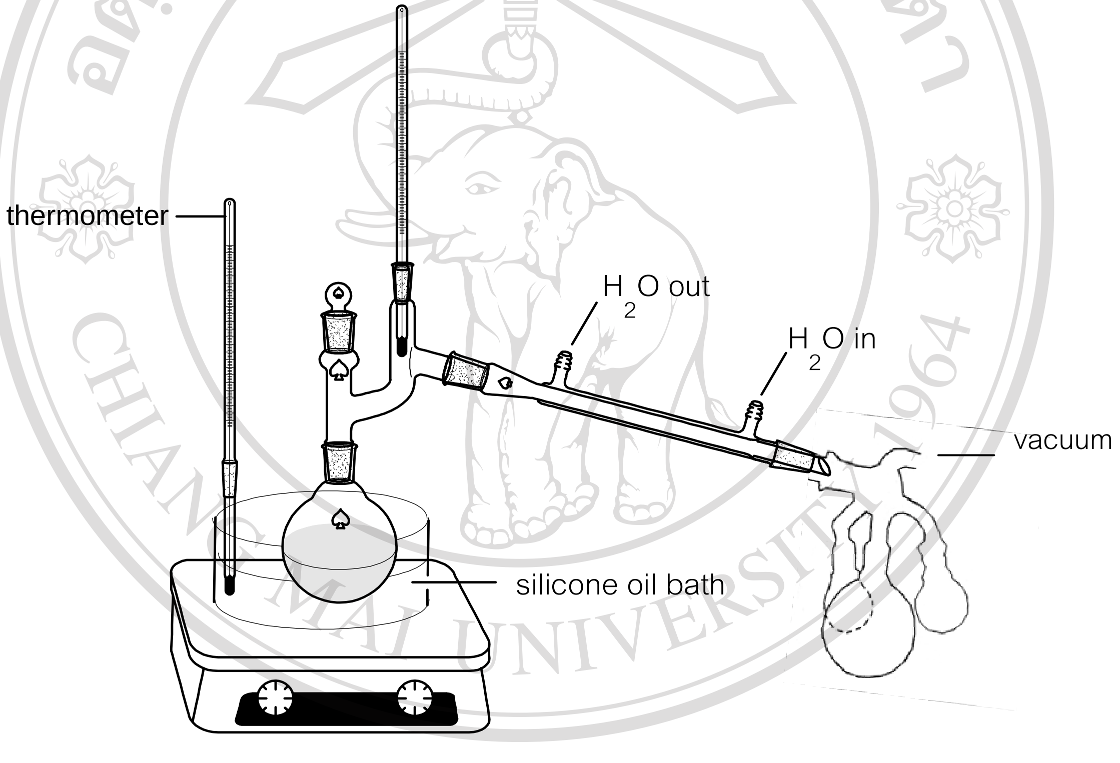


Figure 2.1 Vacuum distillation apparatus used for the purification of $SnOct_2$.

2.3.1.2 Structural Analysis by FT-IR Spectroscopy

The FT-IR spectra of the commercial and purified $SnOct_2$ are compared in Figures 2.2 and 2.3 and Table 2.3.

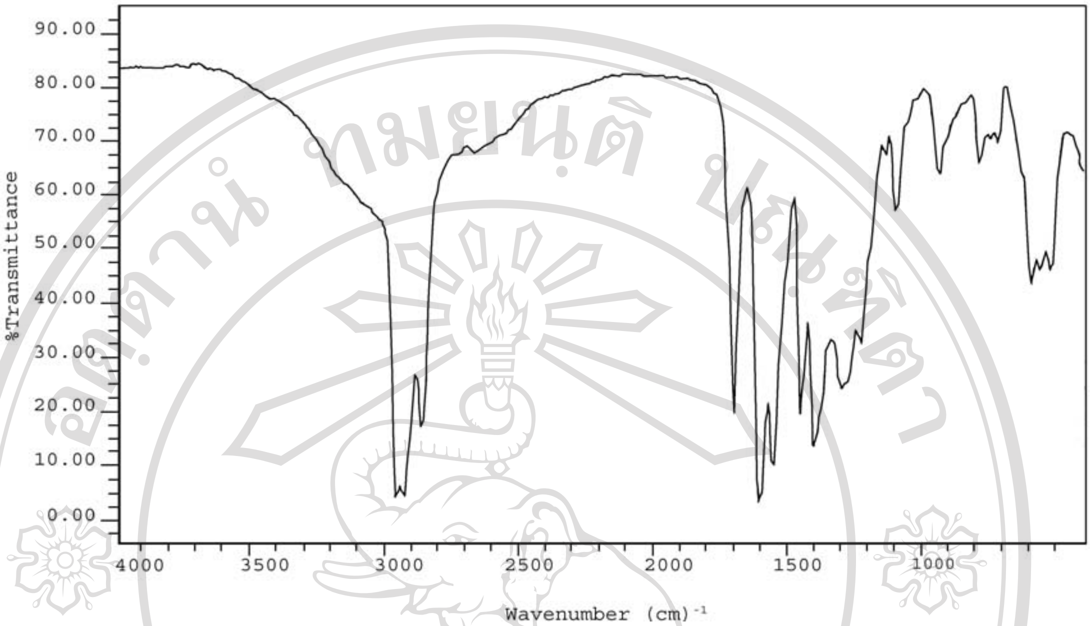


Figure 2.2 FT-IR spectrum of commercial $SnOct_2$ before fractional distillation under vacuum.

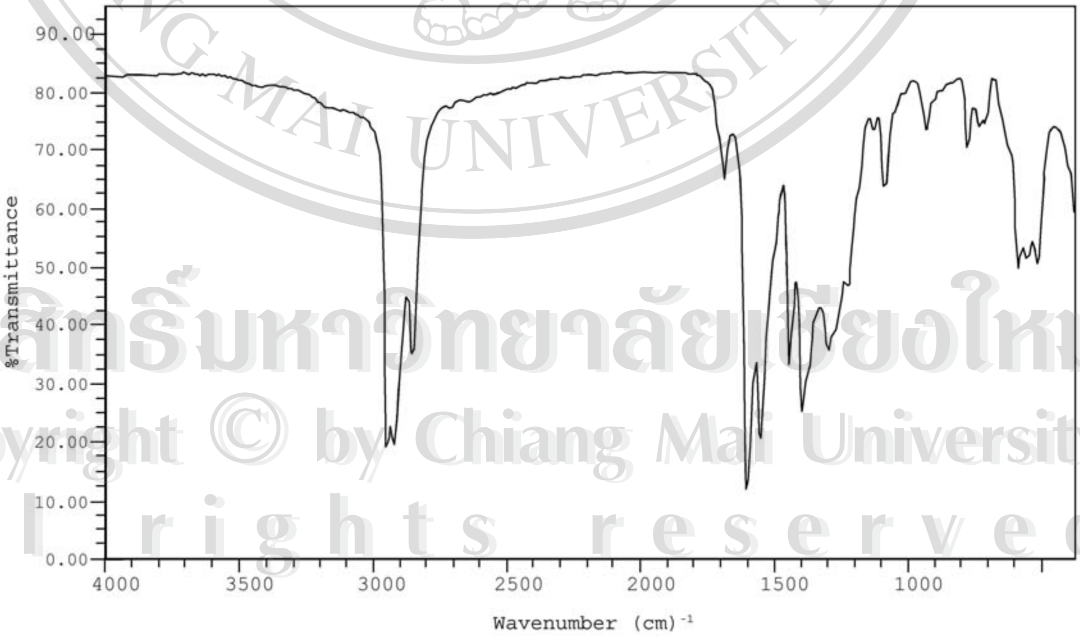


Figure 2.3 FT-IR spectrum of purified $SnOct_2$ after fractional distillation under vacuum.

Table 2.3 Main vibrational assignments for the commercial and purified $SnOct_2$ by FT-IR.

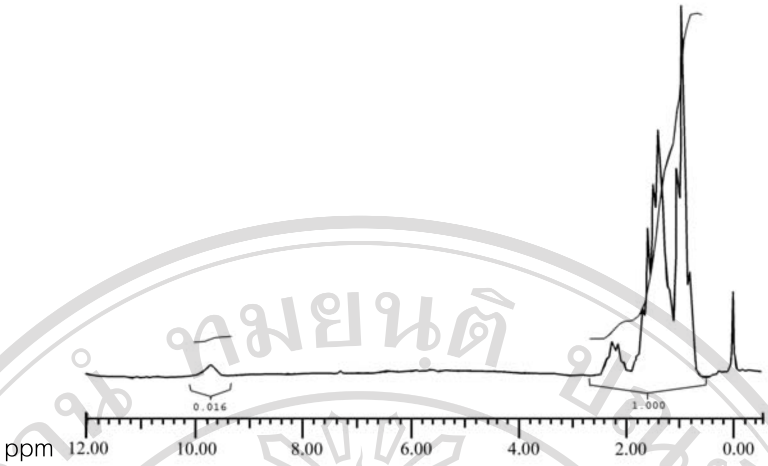
Vibrational Assignment	Wavenumber (cm^{-1})	
	Commercial $SnOct_2$	Purified $SnOct_2$
O-H stretching in COOH	3700-2200 (s)	3700-2200 (w)
C-H stretching	2950-2850 (s)	2950-2850 (s)
C=O stretching (2-ethyl hexanoic acid)	1720 (s)	1720 (w)
C=O stretching ($SnOct_2$)	1600 (s), 1550 (s)	1600 (s), 1550 (s)
C-H bending	1450 (s), 1400 (s)	1450 (s), 1400 (s)
C-O stretching (acyl-oxygen)	1300 (m)	1290 (m)
C-O stretching (alkyl-oxygen)	1230 (m)	1230 (m)

NOTE: peak intensity: (s) = strong, (m) = medium, (w) = weak

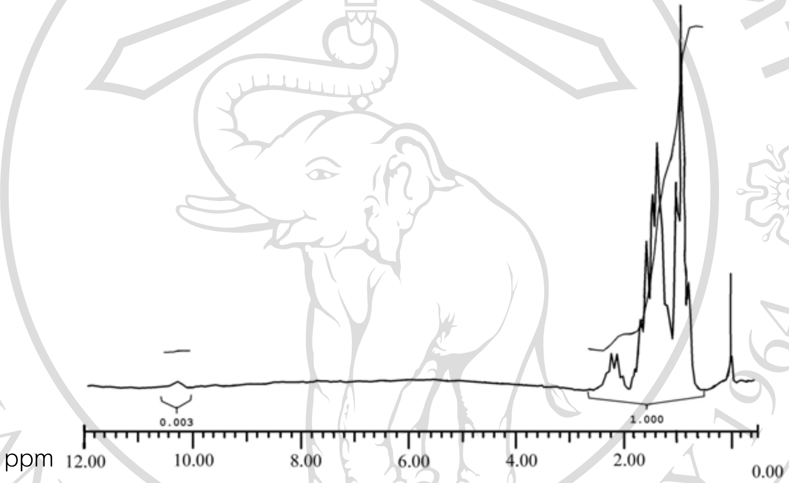
On comparing the FT-IR spectra in Figures 2.2 and 2.3 and Table 2.3, it was found that the 2-ethyl hexanoic acid content in commercial sample are greater than in purified sample, as indicated by the intensity of O-H stretching of carboxylic acid from 3700-2200 cm^{-1} and carbonyl C=O stretching at 1720 cm^{-1}. This is as would be expected due to the fact that the commercial $SnOct_2$ was hydrolyzed by moisture giving 2-ethyl hexanoic acid as a by-product. These results are consistent with the $SnOct_2$ having been successfully purified by fractional distillation.

2.3.1.3 Structural Analysis by ^{1}H-NMR Spectroscopy

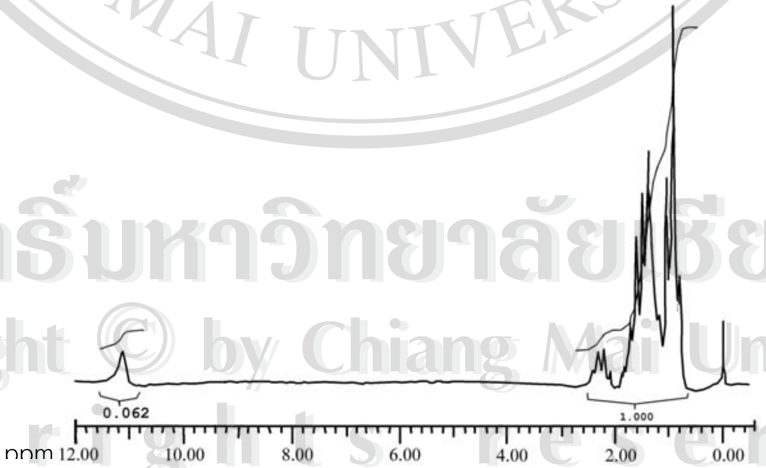
The ^{1}H-NMR spectra of the commercial $SnOct_2$, purified $SnOct_2$ and 2-ethyl hexanoic acid were compared in Figure 2.4 ((a), (b) and (c)) and Table 2.4. The methyl, methylene and methane protons show at δ = 0.5-2.5 ppm. It appears that the 2-ethyl hexanoic acid and water content, as indicated by the presence of the acidic protons (δ = 9.5-11.5 ppm), in purified $SnOct_2$ (Figure 2.4 (b)) was reduced from the commercial sample (Figure 2.4 (a)). Their content compared by the relative intensity of the NMR signal between the protons in alkyl groups and acidic protons.



(a) commercial $SnOct_2$



(b) purified $SnOct_2$



(c) 2-ethyl hexanoic acid

Figure 2.4 ^{1}H-NMR spectra of (a) commercial $SnOct_2$ (b) purified $SnOct_2$ (c) 2-ethyl hexanoic acid.

Table 2.4 ^{1}H-NMR chemical shifts and proton assignments for commercial $SnOct_2$, purified $SnOct_2$ and 2-ethyl hexanoic acid.

Proton Assignment	Chemical Shift, δ (ppm)		
	Commercial $SnOct_2$	Purified $SnOct_2$	Distilled Fraction (2-ethyl hexanoic acid)
CH_3, CH_2 and CH	0.5-2.5 (1)	0.5-2.5 (1)	0.5-2.5 (1)
Acidic Protons	9.5-10.0 (0.016)	10.1-10.2 (0.003)	11.0-11.5 (0.062)

NOTE: figures in brackets refer to the relative peak areas (as given in Figure 2.4)

2.3.1.4 Thermal Characterization by TG Analysis

The TG thermograms of the commercial $SnOct_2$, purified $SnOct_2$ and 2-ethyl hexanoic acid were shown in Figure 2.5. The temperature ranges and the % weight losses can be compared in Table 2.5. The weight loss profile for commercial $SnOct_2$ is seen to be three steps (Figure 2.5 (a)). The water and acid impurities, pure $SnOct_2$ and tin metal are 1st, 2nd and 3rd components, respectively. The tin metal is remaining in the pan because it needs higher temperature for thermal decomposition. After purification, it can be seen clearly to be two step in TG thermogram (Figure 2.5 (b)) that water and acid impurities were removed by distillation under vacuum.

However, all FT-IR, ^{1}H-NMR and TG are not particularly informative technique to confirm the type of removed acid. They need more information from GC-MS to confirm the type of acid impurity.

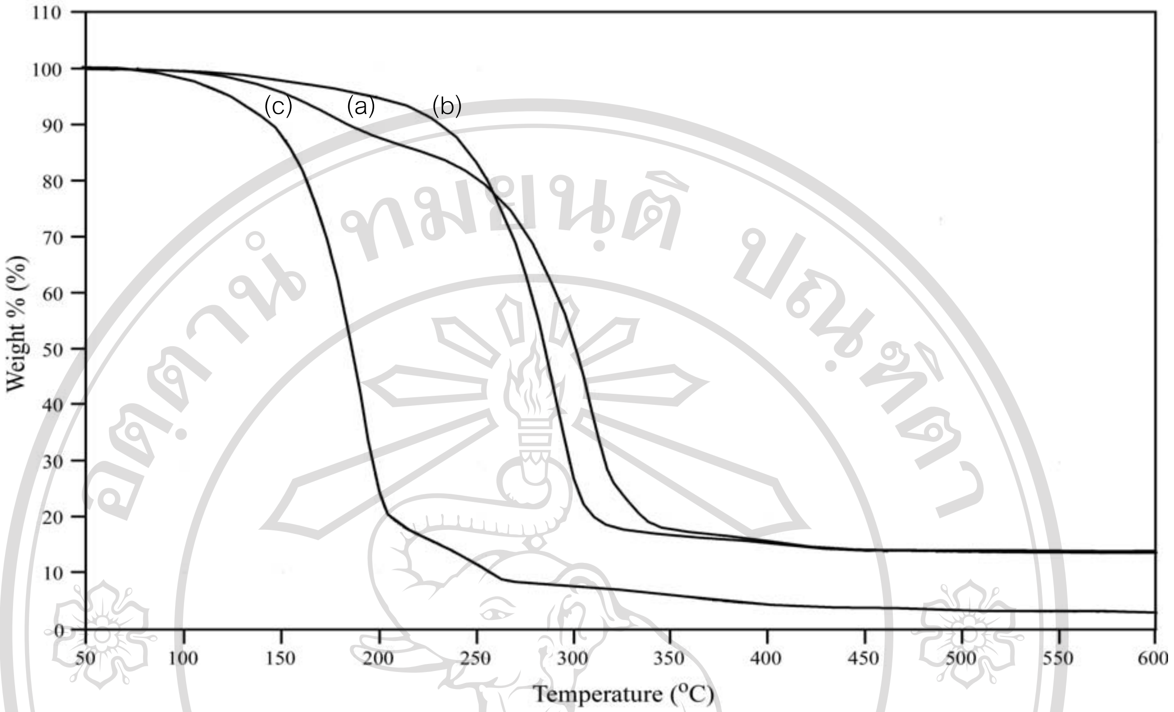


Figure 2.5 TG thermograms of (a) commercial $SnOct_2$ (b) purified $SnOct_2$ (c) 2-ethyl-hexanoic acid.

Table 2.5 Comparison of the temperature ranges for commercial $SnOct_2$, purified $SnOct_2$ and 2-ethyl hexanoic acid.

	Thermal Degradation Temperature (°C)		
Component	Commercial $SnOct_2$	Purified $SnOct_2$	Distilled Fraction (2-ethyl hexanoic acid)
1st component	95-216 (13.8%)	151-400 (88.7%)	87-250 (100%)
2nd component	216-450 (71.4%)	-	-
3rd component	>450 (14.8%)	> 400 (11.3%)	-

NOTE: figures in brackets refer to the (%) weight losses

2.3.1.5 Compositional Analysis by GC-MS Spectroscopy

The GC-MS chromatograms of the commercial $SnOct_2$ is shown in Figure 2.6. Unfortunately, a reference spectrum of $SnOct_2$ was not available. However, the GC-MS chromatogram of distilled fraction as shown in Figure 2.7 is similar to the reference spectrum of 2-ethyl hexanoic acid (Figure 2.8). The GC-MS chromatogram confirmed that the acid impurities is 2-ethyl hexanoic acid. Further information for purified $SnOct_2$ will be required.

The results below supported that impurities both 2-ethyl hexanoic acid and water were eliminated from the distillation of $SnOct_2$ then ensure that $SnOct_2$ used in this research project was pure for ring-opening polymerization.

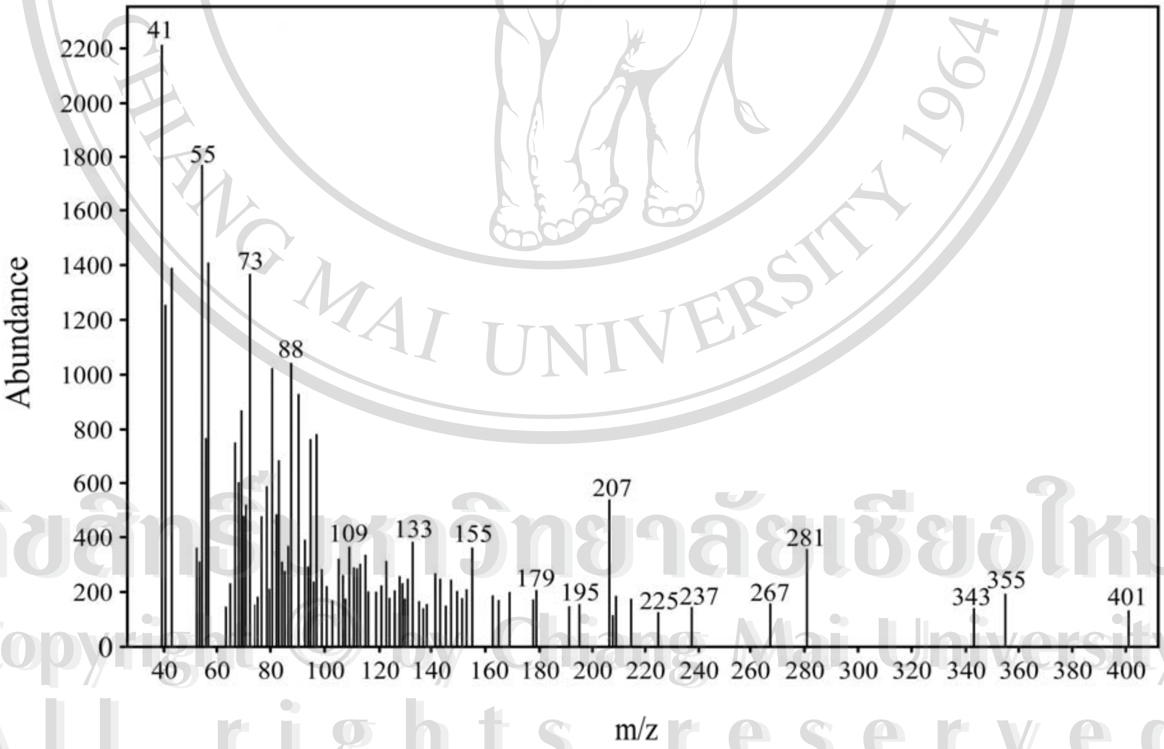


Figure 2.6 MS chromatogram of commercial $SnOct_2$.

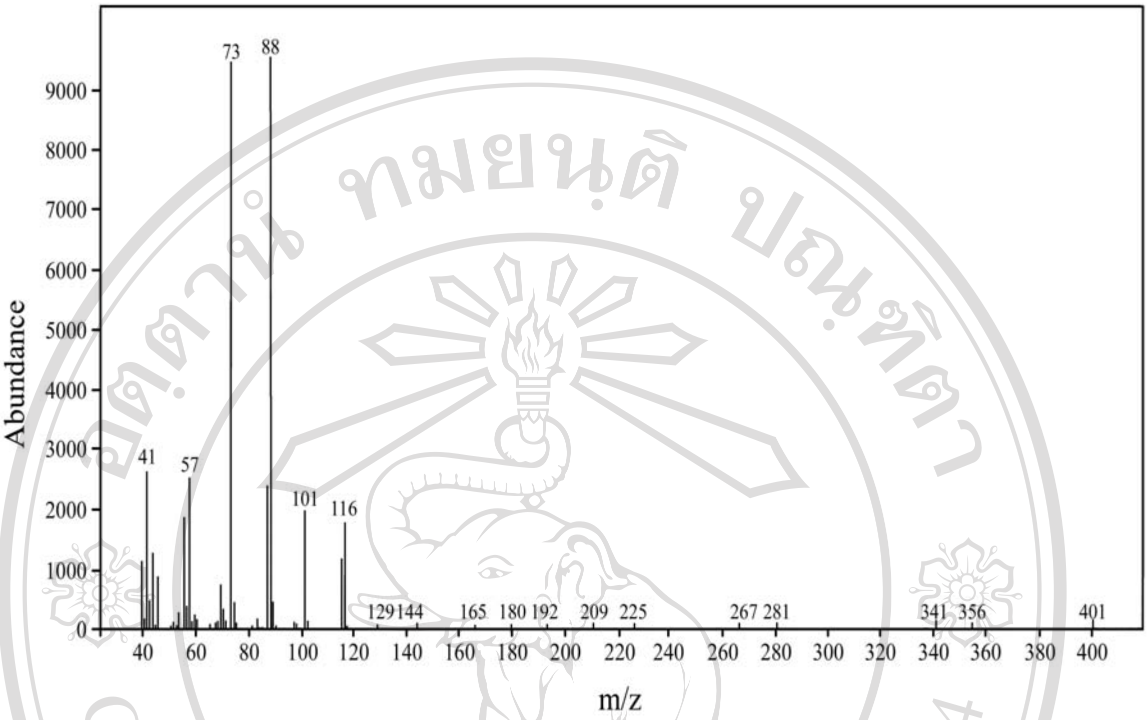


Figure 2.7 MS chromatogram of distilled fraction from $SnOct_2$.

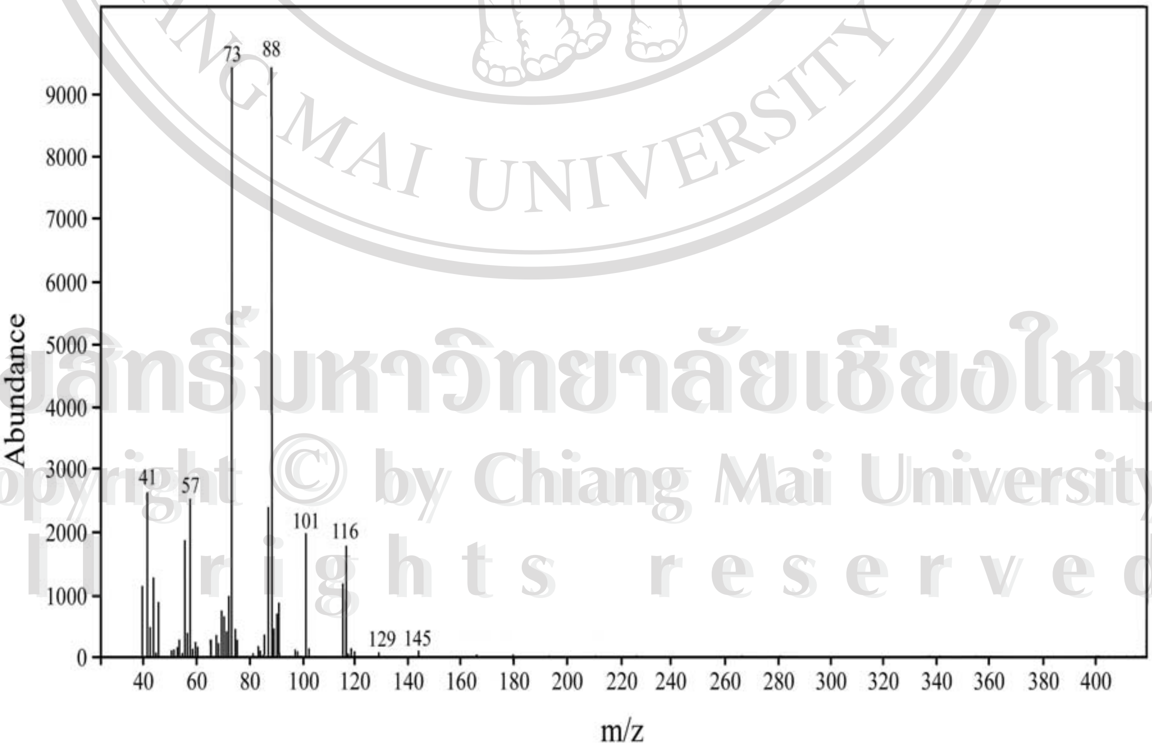


Figure 2.8 MS chromatogram of 2-ethyl hexanoic acid.

2.3.2 1-Hexanol

1-Hexanol, used as monofunctional hydroxyl initiator for the preparation of linear polymers, was purified by vacuum distillation (Figure 2.1). The distilled 1-hexanol was collected as the constant boiling fraction at 47°C/4.0 torr (cf. boiling point = 156°C/760 torr) and then stored over molecular sieves 4 Å.

2.3.3 2,2-Dimethyl-1,3-Propanediol

2,2-Dimethyl-1,3-Propanediol (DMP) the difunctional hydroxyl initiator used in the preparation of linear polymers, was dried to constant weight in a vacuum oven at 60°C to remove any residual moisture traces. Then store in a vacuum desiccator at room temperature. Purity analysis by DSC showed that the purified DMP had a DSC melting peak from 130-131°C, as shown in Figure 2.9, which, when analyzed by the DSC's Purity Analysis Software Program, gave a mole % purity of 99.8%.

The theory of DSC Purity Analysis, which explains the significance of the Van't Hoff plot, is included as an Appendix at the end of this thesis.

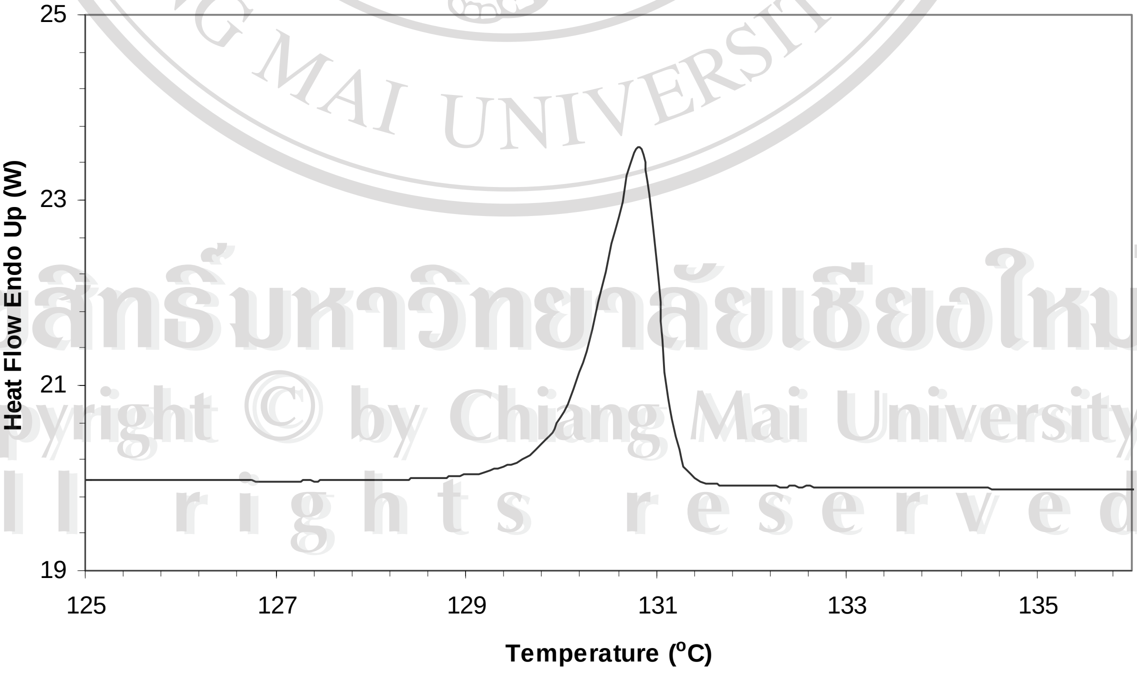


Figure 2.9 DSC thermogram of purified DMP.

2.3.4 1,1,1-Tris(hydroxymethyl)propane

1,1,1-Tris(hydroxymethyl)propane (TMP) used as initiator to yield three-armed star shaped polymers, was recrystallised from dried acetone and subsequently dried under reduced pressure at room temperature until constant weight. Then store in a vacuum desiccator at room temperature. DSC thermogram (Figure 2.10) showed the melting peak from 53-57°C, which, when analyzed by the DSC's Purity Analysis Software Program, gave a mole % purity of 99.9%.

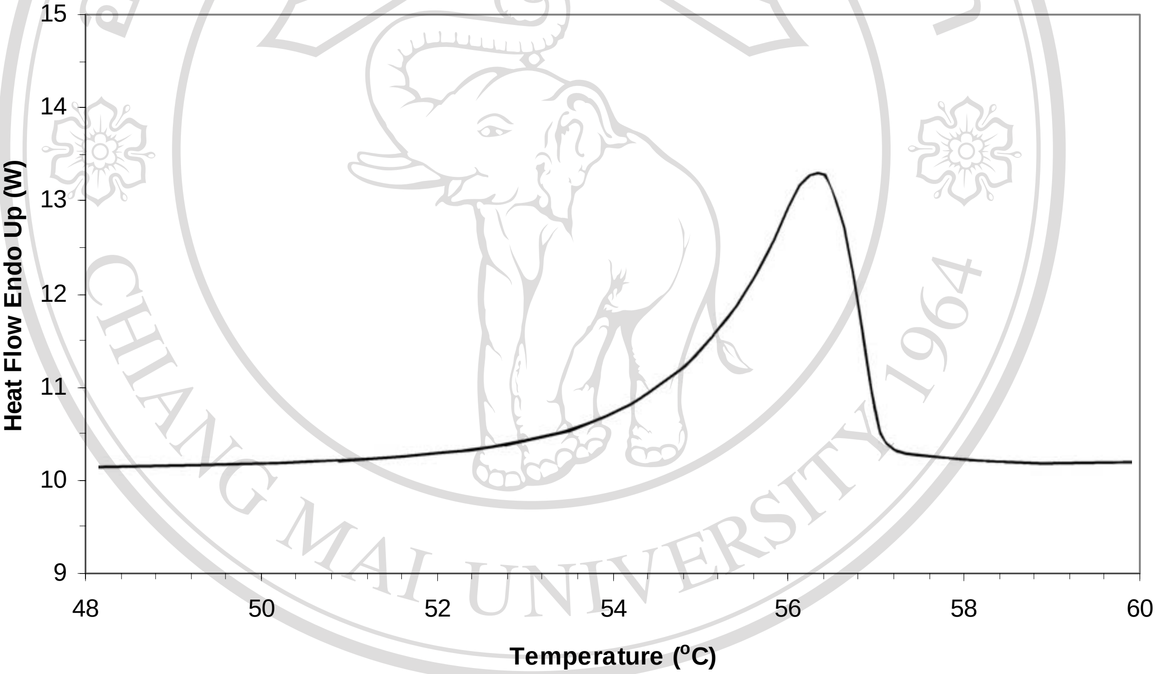


Figure 2.10 DSC thermogram of purified TMP.

2.3.5 Pentaerythritol

Pentaerythritol (PTOL) multifunctional initiator for four-armed star shaped polymer was dried to constant weight in a vacuum oven at 120°C to remove any residual moisture traces. Then store in a vacuum desiccator at room temperature. DSC thermogram (Figure 2.11) showed the melting peak from 252-260°C, which, when analyzed by the DSC's Purity Analysis Software Program, gave a mole % purity of 99.6%.

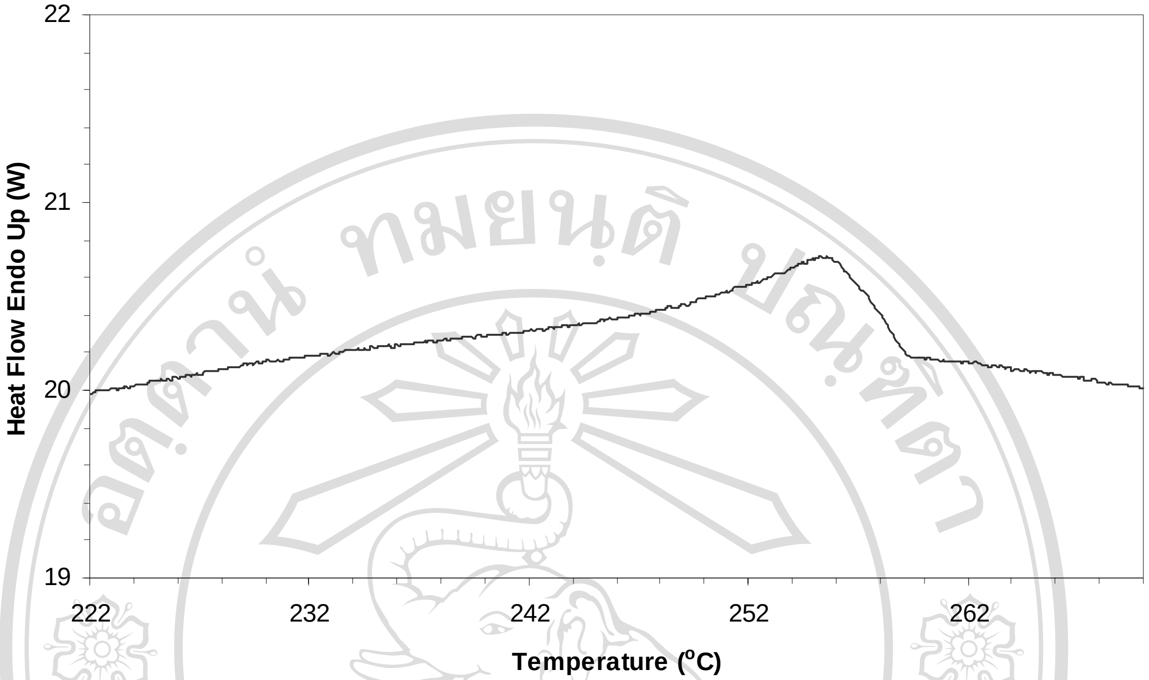


Figure 2.11 DSC thermogram of purified PTOL.

2.4 Monomer Preparation and Purification

The cyclic ester monomers used in this research project were ε-caprolactone and L-lactide. Since L-lactide is prohibitively expensive to buy, it was synthesized from its much cheaper precursor, L(+)-lactic acid. The method of synthesis is described in the following section 2.4.2. 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 polymerization.

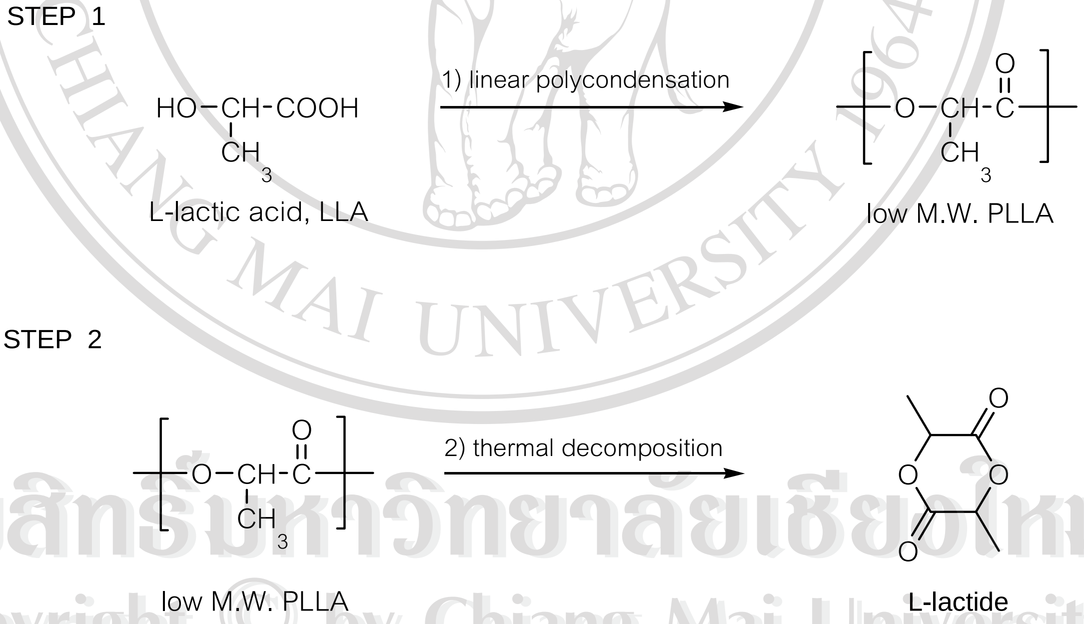
2.4.1 Purification of ε-Caprolactone by Vacuum Distillation

Commercial ε-caprolactone was purified by vacuum distillation (Figure 2.1) before use. Before distillation, the ε-caprolactone was dried over calcium hydride (approximately 1 g/10 ml) by stirring for 1 hour in a closed system. The constant boiling fraction from 72°C/0.8 torr (cf. ε-caprolactone [57] boiling point = 80°C/0.75 torr) being collected. Pure ε-caprolactone was obtained as a clear colorless liquid at room temperature. It was stored over molecular sieve 4 Å in a refrigerator in a tightly sealed container until required for use in polymerization.

2.4.2 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 poly(L-lactic acid) to yield L-lactide as the primary decomposition product, as shown below.

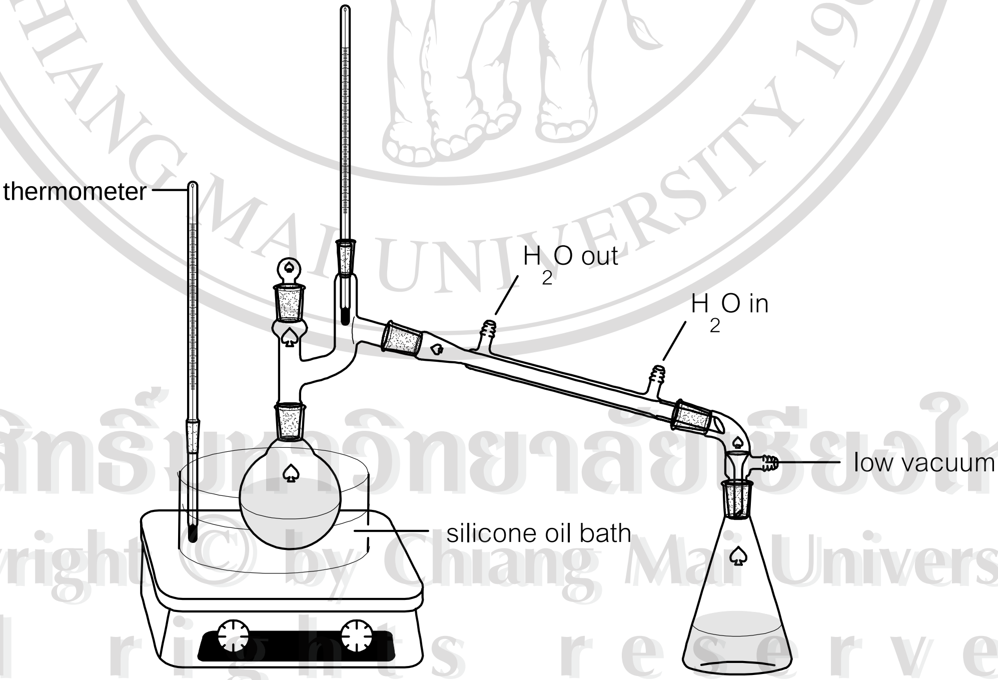
In a typical synthesis reaction in this experiment, approximately 200 g of L-lactic acid were added into a 250 ml round-bottomed flask which contained about 2.0 g of *p*-toluene sulfonic acid (PTSA) as catalyst (1% by weight).



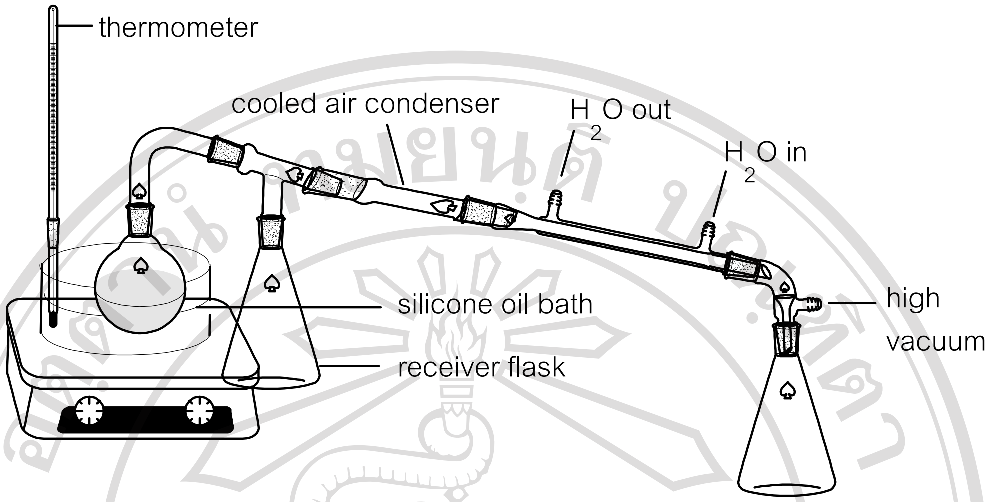
The flask was then heated at 140°C under a nitrogen atmosphere in a conventional short-path distillation apparatus. Heating was continued for about 2 hours before a gentle vacuum was applied to the system for 30 minutes (Figure 2.12 (a)). After that, the temperature was increased to 160°C and kept constant for 3 hours until the water of polycondensation ceased to distill from the reaction flask. The product at this stage was low molecular weight poly(L-lactic acid).

The apparatus was then adapted for vacuum take-off, as shown in Figure 2.12 (b), and antimony trioxide approximately 1% by weight of poly(L-lactic acid) was added as a thermal decomposition catalyst. The reaction temperature was kept constant at 160°C under a reduced pressure of about 2-3 torr for to facilitate further removal of water and so increase the polymer yield.

Finally, for an additional period of about 4 hours, the heating temperature was increased up to 220-250°C to thermally decompose the low molecular weight poly(L-lactic acid) to yield L-lactide as the primary product under the same reduce pressure. Crude L-lactide began to distill out to the receiver flask as a strong yellow crystalline solid in approximately 50-60% yield based on the initial L-lactic acid.



(a)



(b)

Figure 2.12 Apparatus used in the two-step preparation of L-lactide:

(a) L-lactic acid polycondensation to low molecular weight poly(L-lactic acid)

(b) thermal decomposition of low molecular weight poly(L-lactic acid) to L-lactide.

2.4.3 Purification and Purity Analysis of L-Lactide

The crude L-lactide was purified by recrystallisation from distilled ethyl acetate. The purified L-lactide was recovered in approximately 50% as a white, needle-like, crystalline solid. It was dried to constant weight in a vacuum oven at 50°C and stored in this condition until transferred into a glove box for use in synthesis.

Purified analysis by DSC showed that the purified L-lactide had a sharp DSC melting peak from 96-98°C, as shown in Figure 2.13, which, when analyzed by the DSC's Purity Analysis Software Program, gave a mole % purity of 99.9%.

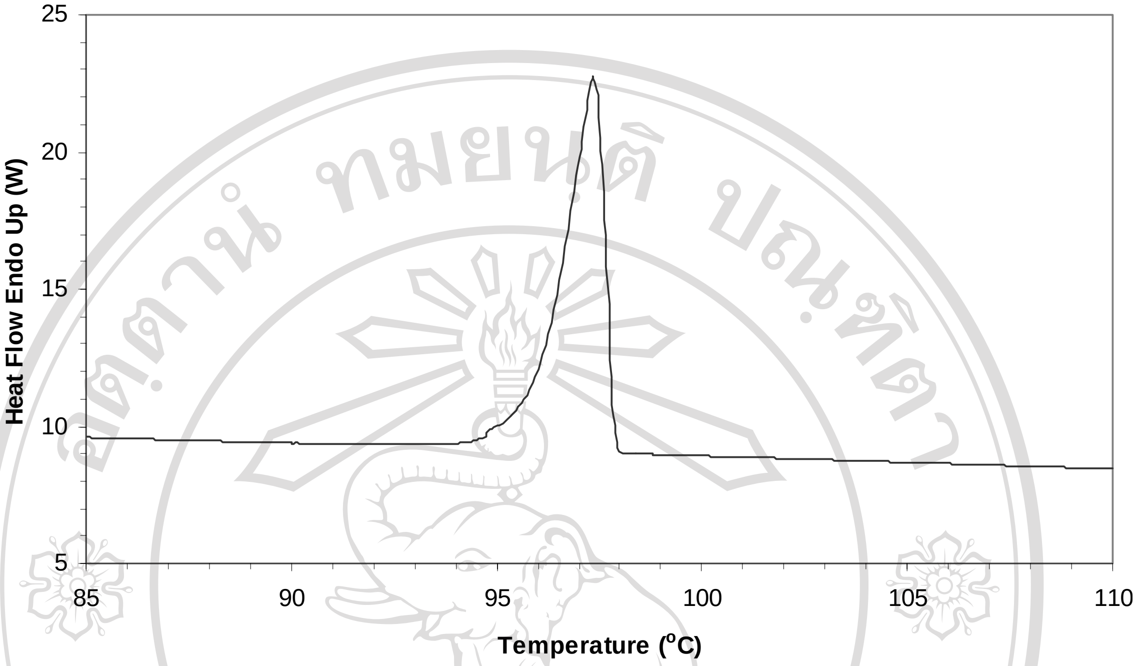


Figure 2.13 DSC thermogram of purified L-lactide after the third recrystallisation.

2.5 Polymer Synthesis

2.5.1 Polymerization Model Reaction

The polymerizations were carried out in closed round-bottomed flasks. A magnetic stirring bar was enclosed in the reaction flask. The equipment was dried in a vacuum oven at 100°C for 48 hours and stored in a glove box purged with nitrogen gas. The monomers and initiators were weighed and added to the reaction flask in the glove box. The desire amount of catalyst was dissolved in dried toluene and transferred to the flask using a syringe. During polymerization, the reaction flask was completely immersed in a thermostated oil bath heated to the polymerization temperature (120°C) for the desired time, see Figure 2.14.

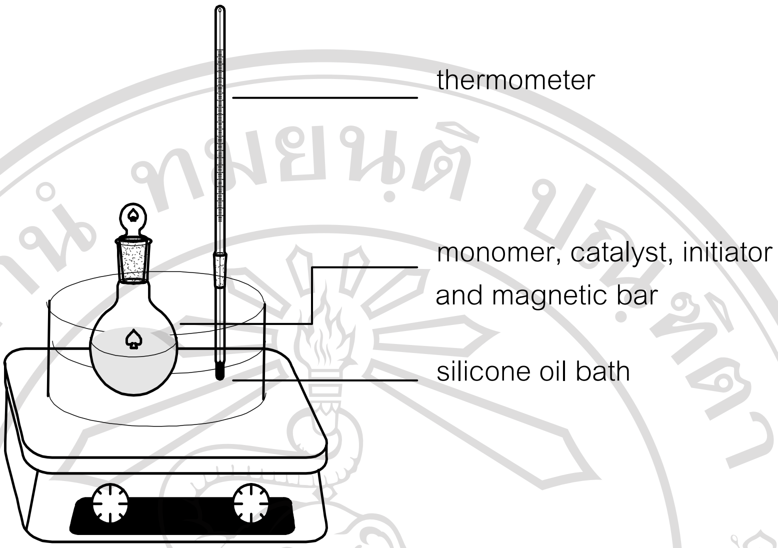


Figure 2.14 Apparatus used for ring-opening polymerization.

2.5.2 Influence of Initiator Concentration on the Poly(ε-caprolactone) Molecular Weight

The synthesis was performed following 2.5.1. ε-Caprolactone was used as monomer. The ratio of catalyst and initiator (total hydroxyl group) was varied from 0.1:10 to 0.1:0.0005 by mole. The reaction was carried out in bulk at 120°C for 48 hours with 1-hexanol as initiator.

2.5.3 Synthesis of Low Poly(ε-caprolactone) with Different Molecular Architectures

The synthesis was performed as earlier. ε-Caprolactone was used as monomer. The ratio of catalyst and initiator (total hydroxyl group) was 0.1:10. The polymerizations were carried out for 48 hours. The oligomers were purified by dissolving in chloroform then reprecipitate in cold hexane (Figure 2.15). The oligomers were collected after drying at 40°C in a vacuum oven until constant weight.

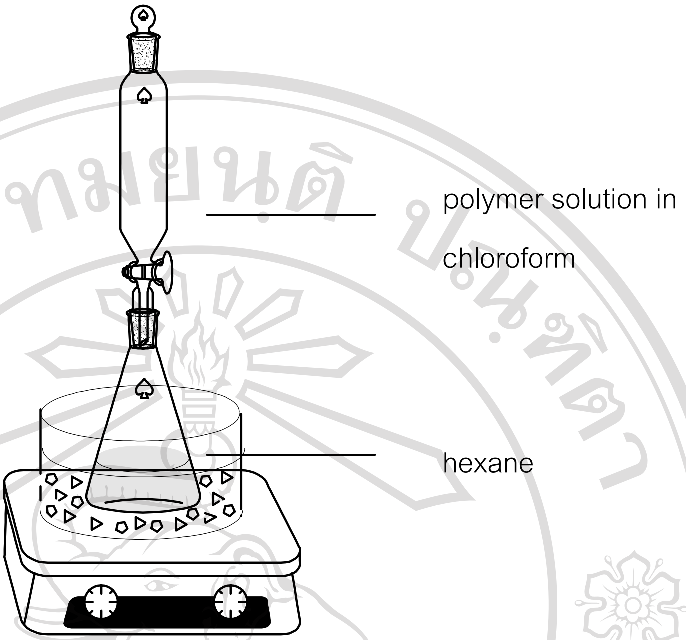


Figure 2.15 Apparatus used for polymer precipitation.

2.5.4 Synthesis of High Molecular Weight Poly(L-lactide-*co*-ε-caprolactone) Copolymers with Different Molecular Architectures

Both ε-caprolactone and L-lactide were used as monomers (50:50 % mole). The ratio of catalyst and initiator (total hydroxyl group) was 0.1:0.2. The polymerizations were carried out for 48 hours and the polymers were purified by drying under vacuum at 60°C for three days.