Chapter 3

Methodology

This work is divided into 3 parts: synthesis, property characterizations and measurement of hydrolytic degradability of PET-co-PLA copolymers. Polycondensation of monomer mixtures was employed in the synthesis, using tin(II)octoate as a catalyst. The copolymers structures and properties are then characterized by NMR, FTIR, DSC and solubility test. Finally, the copolymer degradability is examined by immersing in a buffer solution. The details on the experimental procedures are as follows:

3.1 Materials

- Dimethyl terephthalate (Acros Organics)
- Ethylene glycol (Carlo Erba)
- Propylene glycol (Acros Organics)
- 1, 3-Propanediol (Acros Organics)
- 1, 4-Butanediol (Acros Organics)
- Lactic acid (88wt% in water, Carlo Erba)
- Tin(II)hexylethanoate (Wako)
- Dichloromethane (Lab-scan analytical sciences)
- Trichloroacetic acid (Carlo Erba)

3.2 Equipments

- DSC 2920 Modulated TA Instruments
- NMR, Bruker AC300 (300MHz) spectrometer
- TGA, METTLER TOLEDO STARE SYSTEM
- FTIR, Thermo Nicolet 6700 model spectrometer

3.3 Synthesis of PLA-based Aliphatic-Aromatic Copolyesters

The copolymers were condensation polymerized in a 2-neck round bottom flask under nitrogen atmosphere at 0.2 mbar. 0.2 mol of dimethyl terephthalate (used as received, Acros Organics) and 0.2 mol of Lactic acid (used as received, carlo erloa reagents) were added in the reaction. Tin(II)hexylethananoate (0.5wt% of total reactants including diol) was then added into the mixture. The mixture was stirred at 100 rpm and heated at 150 °C for 1 hour. The mixture was then heated to 200 °C. Subsequently, 0.2 mol of appropriate diols (ethylene glycol, propylene glycol, 1,4-butanediol or 1,3-butanediol) was added by using needle injection under N_2 gas cover surface. The reaction temperature was held at 200 °C for 2 hours, and then raised to 220 °C for 1 hour. An excess 0.2 mol of diol was then added, and the mixture was further heated for 1 hour. By-products from the reaction were condensed and removed by using a vacuum pump at the temperature 220 °C until the total reaction time reach 7 hours. The resulting

copolymers were characterized and used as received. The glassware setup of the reaction is shown in figure 3.1. A graphical illustration of the synthesis procedure is summarized in figure 3.2.
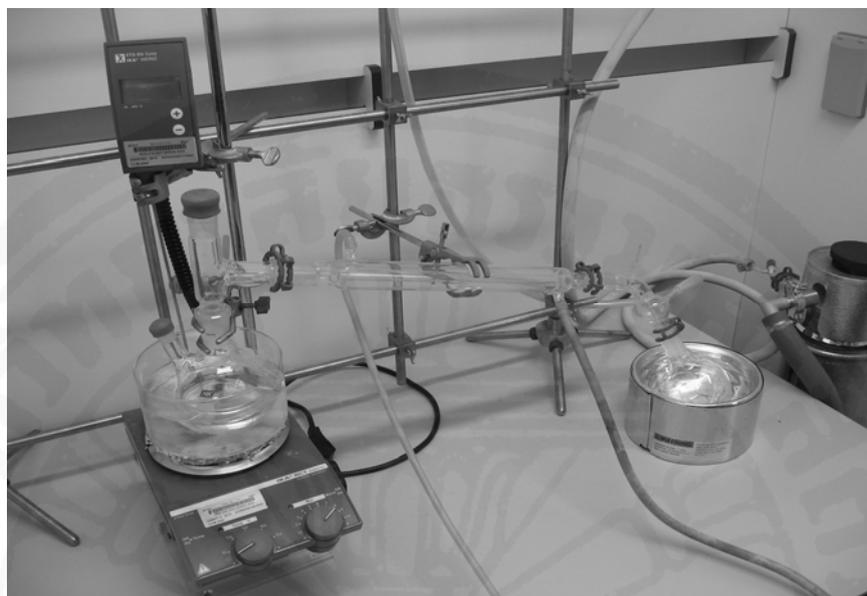
Figure 3.1 The glassware setup for synthesis of the copolymers
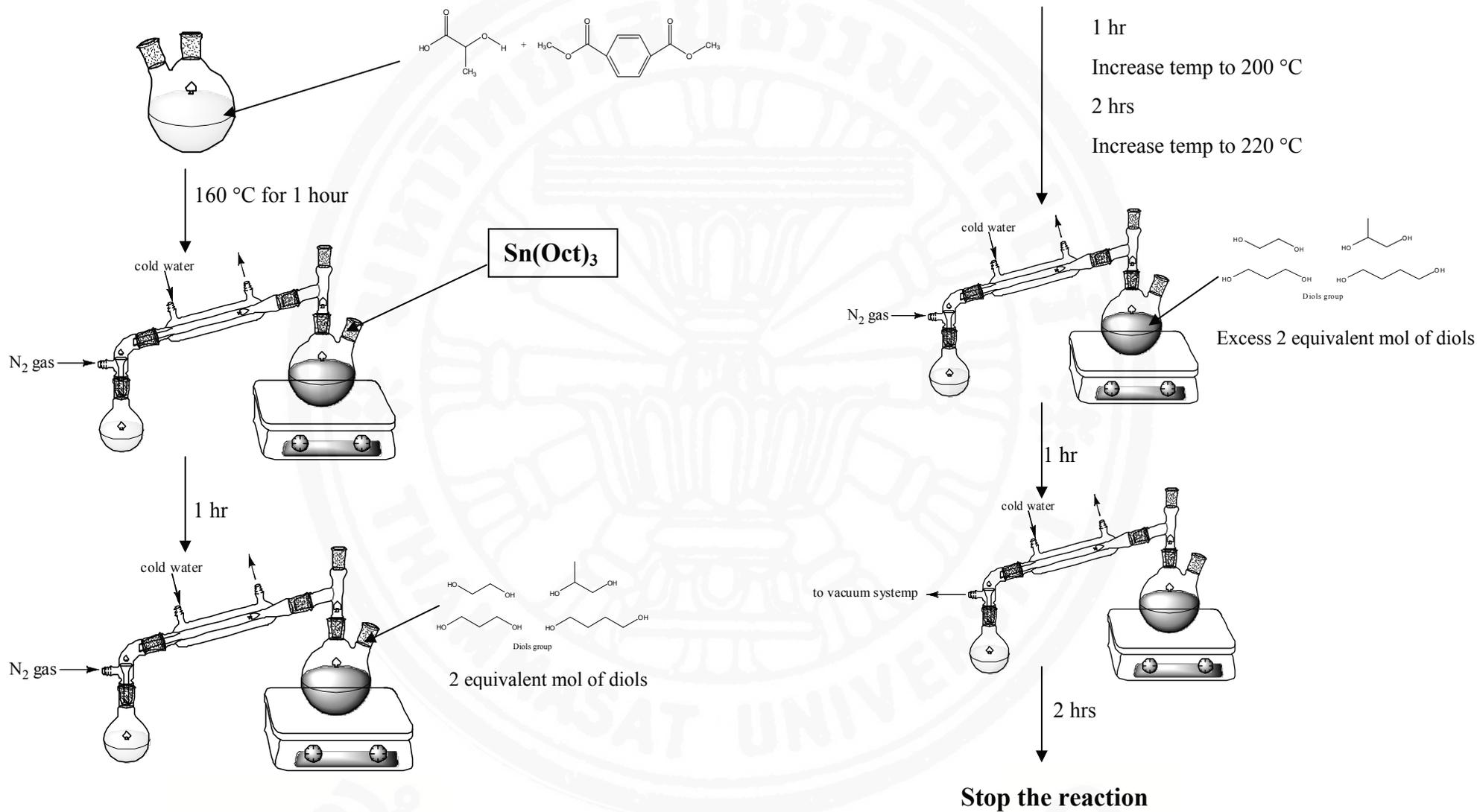
Figure 3.2 A graphical illustration of the synthesis procedure

14

3.4 Characterizations of PLA-based Aliphatic-Aromatic Copolyesters

3.4.1 ^{1}H NMR spectroscopy

^{1}H NMR spectra were recorded on a Bruker AC300 (300MHz) spectrometer, using a 7% wt trifluoroacetic acid /CDCl$_3$ mixed solvent. The spectrum was recorded immediately in order to avoid end-group esterification (E. Olewnik, 2007) by trifluoroacetic acid.

3.4.2 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out under nitrogen on a DSC 2920 Modulated TA Instruments apparatus equipped with liquid nitrogen cooling accessory, at cooling and heating rates of 20 °C/min from 0 °C to 240 °C, using samples of approximately 3–5 mg. Transition temperatures were measured on the second heating curves. Melting temperatures (Tm) were taken at the maxima of melting endotherms and glass transition temperatures (Tg) at the inflection point.

3.4.3 Thermo Gravimetric Analysis (TGA)

TGA analyses were carried out under nitrogen on a METTLER TOLEDO STARE SYSTEM at heating rate of 20 °C/min from 50 °C to 1000 °C using sample of approximately 2.5 mg. The degraded temperature was measured on the mid point of onset.

3.4.4 Fourier-Transform Infrared (FTIR) spectroscopy

FTIR spectra were recorded on a Thermo Nicolet 6700 model spectrometer using a transmission mode. 16 scans were coadded, with a resolution of 2 cm^{-1}. The copolymer sample was prepared into a KBr pellet by mixing with KBr powder.

3.5 Solubility test

The copolymer samples were dissolved in dichloromethane (CH$_2$Cl$_2$) and tetrahydrofuran (THF) at ambient conditions. Essentially, 0.5 g of each copolymer was dissolved in 10 ml of the solvent, and stirred for 15 min. The undissolved portion was then separated from the solution, dried and weighted. The percent of solubility was calculated.

3.6 Degradability of PLA-based Aliphatic-Aromatic Copolyesters

Characterizations of hydrolytic degradability of copolymers were conducted in a phosphate buffer solution (pH 7.2) at 60°C. Essentially, 0.5 g of samples was weighed and placed in a glass vial. The degree of degradation was followed by measuring the percentage weight loss of the samples as a function of time. Separation of supernatant and copolymer powder was done by filtering. The remaining copolymer powder was weighed and the content of the remaining solution was measured in order to have an

insight into changes in chemical structure of the copolymer as a function of the degree of hydrolysis or the percentage weight loss. UV-Vis spectroscopy was employed to the supernatant to examine the content of soluble species in the buffer solution.