

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Reagent

Propionyl chloride (98%, Merck), AlCl₃ (97%, Fluka), Nitrobenzene (98%, Merck), Tin(II) 2-ethylhexanoate (stannous octoate, SnOct₂, Aldrich), LiAlH₄ (99%, Aldrich), Dichloromethane (99.8%, Lab Scan), Tetrahydrofuran (99.8%, Lab Scan), Toluene (99.5%, Lab Scan), Ethanol (99.9%, Aldrich), Dicumyl peroxide (98%, Aldrich), ε-caprolactone (99%, Fluka), DL-lactide (Aldrich), Caprolactam (Thai Caprolactam Public Company Limited), Polystyrene (TPI Polene) were used as received.

3.1.2 Starting Polymers

Polystyrene (MW=238,272.54 in **Table 1**) was cut by dicumyl peroxide 0.5% (w/w) in dichloromethane at room temperature for 10 min and frozen for termination. The molecular weight after chain scission was 77,810.64 determined by SEC.

3.2 Methodology

All syntheses were carried out under purified nitrogen gas.

3.2.1 Synthesis of Ring-Acylated Polystyrene (polymer A)

A dichloromethane solution (180 ml) of polystyrene which was cut (12 g, MW=77810.64, 1.53 mole) was added under nitrogen to a stirred solution of propionyl chloride (10 ml, 0.576 mol), AlCl₃ (12 g) in nitrobenzene (20 ml) (0.09 mol of AlCl₃) and dichloromethane (140 ml). The mixture was stirred for 5 h at room temperature and then precipitated into acidified 80% ethanol (v/v, 1000 ml; 15

ml of HCl). The resulting yellowish product was reprecipitated from THF into 80% ethanol and dried at 40 °C under vacuum (**Figure 3.1A**).

3.2.2 Synthesis of Polystyrene Ring Substituted with 1-Hydroxypropyl Group (polymer B)

A solution of polymer A (10 g, 1.22 mol) in dry THF (160 ml) was added to a suspension of LiAlH_4 (10 g, 0.26 mol) in dry THF (340 ml) under nitrogen gas. The mixture was refluxed for 5 h and, after that water (5 ml) was gently added to decompose residual LiAlH_4 . The mixture was then precipitated into acidified water (1350 ml; 150 ml of HCl), filtered, washed with water and dried. The product was reprecipitated from THF into water and finally dried at 40 °C under vacuum (**Figure 3.1B**).

3.2.3 Synthesis of Polystyrene-Graft-Poly(ϵ -caprolactone)

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 1.20 mol), and ϵ -caprolactone (1 g, 2 g, and 3 g; ratio 1:1, 1:2 and 1:3, respectively) in toluene (10, 20 and 30 ml respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3 mmol or 0.12153 g of SnOct_2 , MW = 405.10) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum (**Figure 3.1C**).

3.2.4 Synthesis of Polystyrene-Graft-Poly(DL-lactide)

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 1.20 mol), and DL-lactide (1 g, 2 g, and 3 g; ratio 1:1, 1:2 and 1:3, respectively) in toluene (10, 20 and 30 ml, respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3mmol or 0.12153 g of SnOct_2 , MW = 405.10) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum (**Figure 3.1D**).

3.2.5 Synthesis of Polystyrene-Graft-Polycaprolactam

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 1.20 mol), and caprolactam (1 g, 2 g, and 3 g; ratio 1:1, 1:2 and 1:3, respectively) in toluene (10, 20 and 30 ml, respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3 mmol or 0.12153 g of SnOct₂, MW = 405.10) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum (**Figure 3.1E**).

3.3 Equipment and Characterization

3.3.1 NMR

¹³C and ¹H NMR spectra were used to analyze the resulting polymers that were dissolved in CDCl₃ in 5-mm glass tubes using a Bruker DPX 300 spectrometer at frequencies 75.4 and 300.1 MHz, respectively, with an internal deuterium lock. The number of data points was 32,000, repetition delay 5-10 s, temperature 297 K and the number of FID accumulations was 32-12,000 to obtain a good signal-to-noise ratio. ¹³C NMR spectra were measured using a standard pulse sequence with inverse gated decoupling. Hexamethyldisiloxane was used as an internal standard for calibration of the ¹³C and ¹H NMR scale, the chemical shifts of the nuclei being 2.0 and 0.05 ppm, respectively, referred to tetramethylsilane.

3.3.2 FTIR/HATR Spectroscopy

FTIR spectra were obtained with a Thermo Nicolet spectrometer (NEXUS 670 FT-IR). The spectra were collected in the wave number ranging from 4000-400 cm⁻¹ and using sample-KBr pellets. For HATR (spectra-Tech) measurements, a ZnSe crystal ($\theta = 45^\circ$, $n_p = 2.4$) was used. All spectra were recorded at a resolution of 2 cm⁻¹. The samples for HATR were dissolved in THF. A few drop of the solution was allowed to spread out over the surface of the window. After solvent evaporation, the single window was placed in a demountable cell and a reflectance spectrum was taken. Reflectance spectra were converted to absorbance

spectra, and a base line drift was removed using the instrument software (OMNIC) (Dubis, *et al.*, 1999).

3.3.3 Differential Scanning Calorimetry

The melting temperature and the melting enthalpy (ΔH_m) were determined by differential scanning calorimetry (DSC). The melting points were defined as the peak of the endothermal curve. The DSC measurements were carried out with a Perkin-Elmer DSC7 differential scanning calorimeter under N₂ purge (flow rate = 1 ml/min.), at heating rate 10°C/min. The temperature and heating flow calibration were performed with indium. The scanning range was from 25-350 °C.

3.3.4 UV-Visible Spectroscopy

DR-UV absorption spectra were recorded on a SHIMADZU UV-2550 UV-Visible Spectrophotometer. The spectra were corrected for the wavelength dependence on the instrumental response. The sample was in solid state, next, it was compress in specific mold for UV-visible spectroscopy.

3.3.5 Gel Permeation Chromatography (GPC)

All polymers were characterized by GPC (WATERS 600E System Controller) in THF at room temperature at flow rate of 1 ml/min using Water Styragel™ HR 5E column (7.8x300 mm, Serial Number T41921A 03 and Part No. WAT044228 MILLIPORE, Effective molecular weight range = 2,000 – 4 x 10⁶) and RI(WATER 410) detectors. Polystyrene standards for PS/THF system were used to calculate apparent values of molecular weights and molecular weight distributions (MWD). Samples were dissolved in THF, their concentrations were about 0.5 %(w/v).

In part of solubility, the molecular weight of polymer fractions that were dissolved in water was characterized by GPC (SHIMADZU) on condition at room temperature, pressure 1 MPa at flow rate 1 ml/min using water as eluent. The GPC composed of degasser (DGU-12A), system controller (SCL-10Avp), column oven (CTO-10Avp), liquid chromatograph (LC-10ADvp), refractive index detector (RID-10A), and fraction collector (FRC-10A). OHPak SB-803 HQ, OHPak SB-804

HQ, and OHPak SB-806 HQ were the columns that connect in this machine, their exclusion limit (PEG) were in the range of 5.5×10^4 - 1×10^5 , 3×10^5 - 1×10^6 , and 1×10^7 - 2×10^7 , respectively. Characteristic of columns were column size (8 mmx300 mm), column material (polyhydroxymethylmethacrylate gel), and in-column solvent (0.02% sodium azide). Glucose standards for Glucose/water system were used to calculate apparent values of molecular weights and molecular weight distributions (MWD).

3.3.6 Total Organic Carbon Analyzer (TOC-V_{CSH})

The carbon quantity of polymers that were dissolved in water after 24 h was recorded on TOC (SHIMADZU and ASI-V SHIMADZU). Injection volume is 10 μ l and the maximum calibration is 2000 mg/l. (Tomita *et.al.*, 2004)

3.3.7 Thermal Gravimetry - Dynamic Temperature Analysis (TG-DTA)

Thermal Gravimetry - Dynamic Temperature Analysis technique was used to determine thermal stability and the decomposition temperature of graft copolymers. Perkin-Elmer thermal gravimetry - dynamic temperature analyzer was used to characterize graft copolymers at heating rate 10 °C/min under the nitrogen atmosphere. The mass change with increasing temperature was monitored and recorded. The decomposition temperature (T_d) was obtained from the derivative TG-DTA thermogram. The samples were in solid state.

3.3.8 Dynamic Mechanical Thermal Analyzer

A DMTA V (Rheometric Sciencetific) was used to measure the storage and loss moduli of the graft copolymers as a function of temperature using compression mode (apply load = 0.01 N). Specimen dimensions were approximately 10 mm diameter. All tests were performed at a frequency of 1 Hz, a strain of 0.1 and 30-130 °C.

3.3.9 Solubility

Sample was put in glass tube, then, solvent (water, chloroform, 0.1 wt% salt water, methanol, propanol, or acetic acid (pH 4)) was gently dropped to

sample until samples was totally dissolved. Volume of drops of solvent was determined by cylinder.

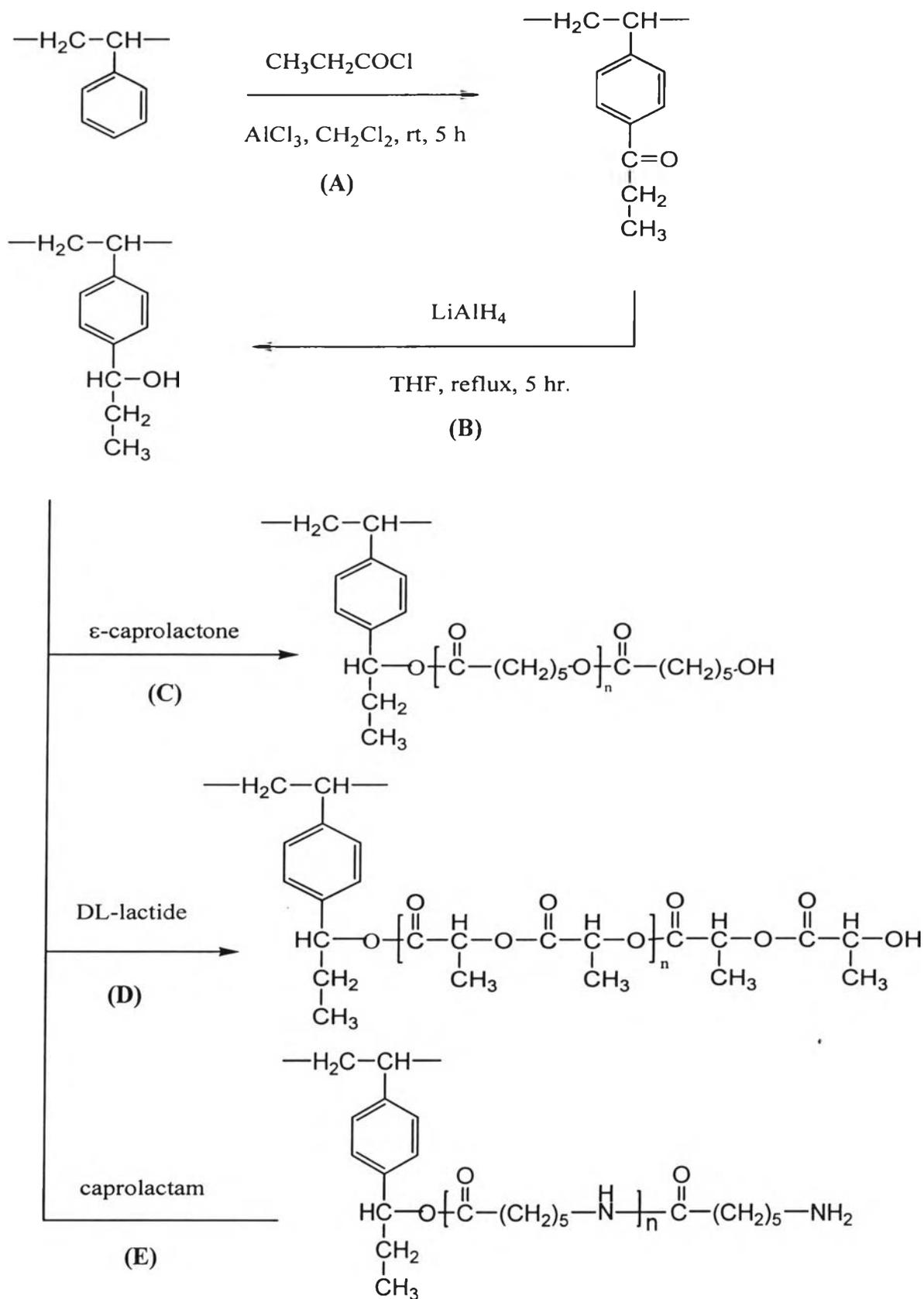


Figure 3.1 Synthesis method.