

## CHAPTER III EXPERIMENTAL

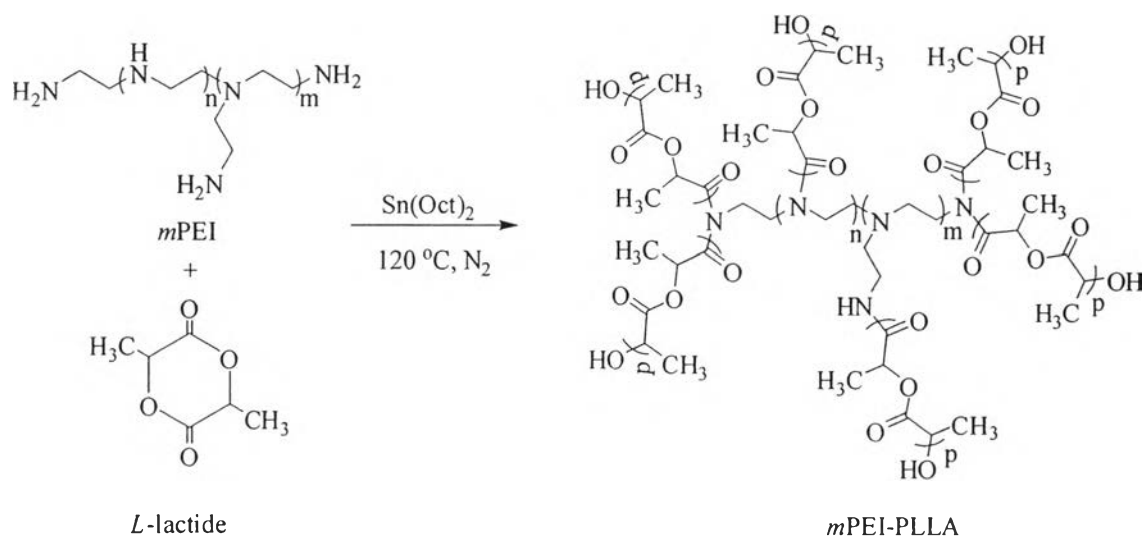
### 3.1 Materials

Multi-branched polyethyleneimine (*m*PEI, MW 25,000 g mol<sup>-1</sup>) was obtained from Sigma-Aldrich. All other chemicals (Sigma-Aldrich) were used without further purification. It was dried under vacuum at 80 °C for 3 hours before use. Tin(II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>, 97% purity), analytical-grade chloroform, deuterated chloroform (CDCl<sub>3</sub>), ethyl acetate and diethyl ether were bought from Sigma-Aldrich and used directly. L-lactide was kindly provided by PTT Public Company Limited. Commercial PLA (2002D) was purchased from Natureworks LLC. HPLC-grade chloroform was from RCI Labscan.

### 3.2 Methodology

#### 3.2.1 Preparation of Multi-branched Polyethylenimide-co-poly(lactic acid)

Multi-branched polyethylenimide-co-poly(lactic acid) (*m*PEI-PLLA) was synthesized through ring-opening polymerization of *L*-lactide (*L*-LA) and polyethylenimide (*m*PEI) by using tin octoate Sn(Oct)<sub>2</sub> as a catalyst (Figure 3.1). The ring-opening polymerization was carried out at 120 °C for 4 h under nitrogen atmosphere. The product obtained was dissolved in chloroform and precipitated in diethyl ether before drying under vacuum at 60 °C for 24 h. The molar feed ratios of *m*PEI to *L*-lactide 1:166, 1:415, 1:830, 1:1162, 1:3320 and 1:6640 were used to obtain *m*PEI-PLLA<sub>3</sub>, *m*PEI-PLLA<sub>5</sub>, *m*PEI-PLLA<sub>10</sub>, *m*PEI-PLLA<sub>14</sub>, *m*PEI-PLLA<sub>40</sub> and *m*PEI-PLLA<sub>80</sub>, respectively.



**Figure 3.1** Synthesis and molecular structures of *m*PEI-PLLAs.

### 3.2.2 Preparation of PLA/*m*PEI-PLLA<sub>n</sub> Blend Films

Commercial PLA was blended with *m*PEI-PLLA by solution casting method. PLA (2002D commercial grade) (0.5 g) and *m*PEI-PLLAs (10, 20, and 30%) were dissolved in chloroform 15 ml. The solution was mixed under vigorous stirring for approximately 4 h. The solution was casted on petri-dish, and then the solvent was evaporated at room temperature for 48 h and further dried under vacuum for 48 h.

## 3.3 Characterization

### 3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained from an FTIR spectrophotometer (Bruker EQUINOX 55) with 32 scans at a resolution of  $4\text{ cm}^{-1}$  and wavenumber range of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . The spectra were acquired and manipulated with OPUS software.

### 3.3.2 Nuclear Magnetic Resonance (NMR)

NMR spectra were obtained from a Bruker Ultrashield 500 Plus (500 MHz). The samples were dissolved in deuterated chloroform ( $\text{CDCl}_3$ ).

### 3.3.3 Gel Permeation Chromatography (GPC)

Molecular weight and polydispersity were determined by a Shimadzu size-exclusion chromatograph (SEC) equipped (Polymer Laboratories, Varian Inc.) and a refractive index detector. Chloroform was used as an eluent at a flow rate of  $1.0 \text{ mL min}^{-1}$ . Polystyrene standards were used and measurement was performed at  $40 \text{ }^\circ\text{C}$  with  $20 \text{ }\mu\text{L}$  injection volume.

### 3.3.4 Differential Scanning Calorimeter (DSC)

Differential scanning calorimetry (DSC) measurement was performed on 5-10 mg samples under nitrogen atmosphere by using a NETZSCH-Proteus differential scanning calorimeter. Samples were heated from  $-70$  to  $200^\circ\text{C}$  and then cooled to  $-70^\circ\text{C}$  with  $10^\circ\text{C}/\text{min}$ . After that they were heated again to  $200$  at  $5^\circ\text{C}/\text{min}$  ( $2^{\text{nd}}$  heating scan). Glass transition temperature was measured from the inflection point in the  $2^{\text{nd}}$  heating thermogram. Crystallization and melting enthalpies changes were determined from integral of their peaks.

### 3.3.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) technique was applied for 10-15 mg samples either under nitrogen atmosphere or under air with a Perkin Elmer Pyris Diamond. All samples were heated from  $50$  to  $700 \text{ }^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . Degradation temperature at 5% weight loss ( $T_d$ ) and the mass residue at  $600 \text{ }^\circ\text{C}$  (WR 600) were measured in this study.

### 3.3.6 Scanning Electron Microscope (SEM)

Morphology of cross-section surface of film specimens was observed under a scanning electron microscope (SEM, Hitachi, S-4800). The samples were put on the holder with an adhesive tape and coated with a thin layer of platinum for 1 min.

### 3.3.7 Mechanical Properties

The mechanical properties of the PLA/*m*PEI-PLLA<sub>n</sub> blends films were investigated by a universal testing machine (Lloyd). The yield setup mode was used

with preload of 0.1 N, a speed of 50 mm/min, and a gauge length of 50 mm. All films were under vacuum system before tensile test. The values of stress at break and elongation at break were reported. The sample was determined through different parameters (Chivrac *et al.*, 2006).

#### 4.3.8 Crystallization Behavior

The crystallization behavior and spherulite morphology of PLA and PLA/*m*PEI-PLLA films were observed by a Leica DMRXP polarizing optical microscope (POM) equipped with a Mettler Toledo FP90 central processor hot stage. Each film was heated from 25 °C to 200 °C at 20 °C min<sup>-1</sup> before kept at 200 °C for 2 min to allow complete melting, and then subjected to another hot stage at 110 °C to observe spherulite formation.