

CHAPTER III

EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer. Anhydrous ferric chloride, FeCl_3 (AR grade, Riedel-delHean) was used as the oxidant. Chloroform, CHCl_3 (AR grade, Lab-Scan), methanol, CH_3OH (AR grade, Lab-Scan) and Dimethyl sulfoxide (DMSO) are dried over CaH_2 for 24 hours under the nitrogen atmosphere and then distilled, were used as solvents. The perchloric acid dopant, HClO_4 (AR grade, AnalaR) was used as received. Sulfuric acid, H_2SO_4 was used to protect the oxidative decomposition of monomer. Diethyl ether and deionized water were used to extract and wash materials. Sodium hydroxide, NaOH was used as the hydrolyzing agent. Polyisoprene, PI ($M_w = 40,000$, viscosity = 400 poise, Aldrich), was used as the polymer matrix. Dicumyl peroxide (AR grade, Fluka) was used as the crosslinking agent.

3.1.2 Instruments

A Fourier Transform Infrared Spectrometer (Thermo Nicolet, Nexus 670) with number of scans of 32, A UV-Visible absorption spectrometer (Perkin Elmer, Lambda 10), Thermalgravimetric analyzer (DuPont, model TGA 2950) with the temperature scan from 30 to 800°C with a heating rate of 10°C/min under O_2 atmosphere were used to characterize the synthesized polythiophene and polythiophene/polyisoprene blends. A Mettler-Toledo DSC822 differential scanning calorimeter (DSC) was used to record the nonisothermal exotherms as well as the subsequent melting endotherms for crosslinked polyisoprene (PI_03), undoped polythiophene (Pth_U), and polythiophene/polyisoprene blends (Pth_U/PI_03). Scanning electron microscope (JOEL, model JSM-5200-2AE) was used to determine the morphological structure of the synthesized polymers and polymer blends with the magnifications of 350,750 and 1500 times at 20 kV. Custom-built two-point probe electrometer (Keithley, Model 6517A) was used to measure electrical conductivity of

the conductive polymer. Melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological properties. DC power supply (Instek, GFG 8216A), which can deliver electric field strength to 2 kV/mm.

3.2 Experimental Methods

3.2.1 Polymerization Procedure

3.2.1.1 *Preparation of 3-Thiophene Methyl Acetate (TMA)*

The reaction was by oxidative-coupling polymerization according to the method of Kim *et al.* (1999). 10.0 g of 3-thiopheneacetic acid was refluxed for 24 hours in 50 ml of dry methanol with 1 drop of concentrated H₂SO₄ in order to protect the oxidative decomposition of the carboxylic acid group of monomer during oxidative-coupling polymerization. The methanol was evaporated, and the residue was extracted with fresh diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO₄ and then filtered. The diethyl ether was evaporated from the filtrate by rotating evaporator. TMA product was obtained.

3.2.1.2 *Synthesis of Poly(3-Thiophene Methyl Acetate) (P3TMA)*

In a 100 ml three-necked flask, a solution of 10 mmol of protected monomer in 20 ml of chloroform was added dropwise to a solution of 40 mmol of ferric chloride was dissolved in 30 ml of dry chloroform under nitrogen atmosphere. The molar ratio of the oxidant to monomer is 4:1 in all cases. The reaction was carefully maintained at 0°C ($\pm 0.5^\circ\text{C}$) for 24 hours. The reaction mixture was precipitated, by pouring into a large excess amount of methanol (1 L) to obtain P3TMA. The product was repeatedly washed with methanol and deionized water.

3.2.1.3 *Synthesis of Poly(3-Thiopheneacetic acid) (P3TAA)*

PTMA was hydrolyzed as follow; 0.5 g of P3TMA was dissolved in 50 ml of 2.0 M NaOH solution and heated for 24 hours at 100°C. The mixture was filtered, neutralized and precipitated with a dilute HCl solution (~0.5 M) to obtain polymer product. The PTAA was washed several times with deionized water before vacuum drying at room temperature for 2 days.

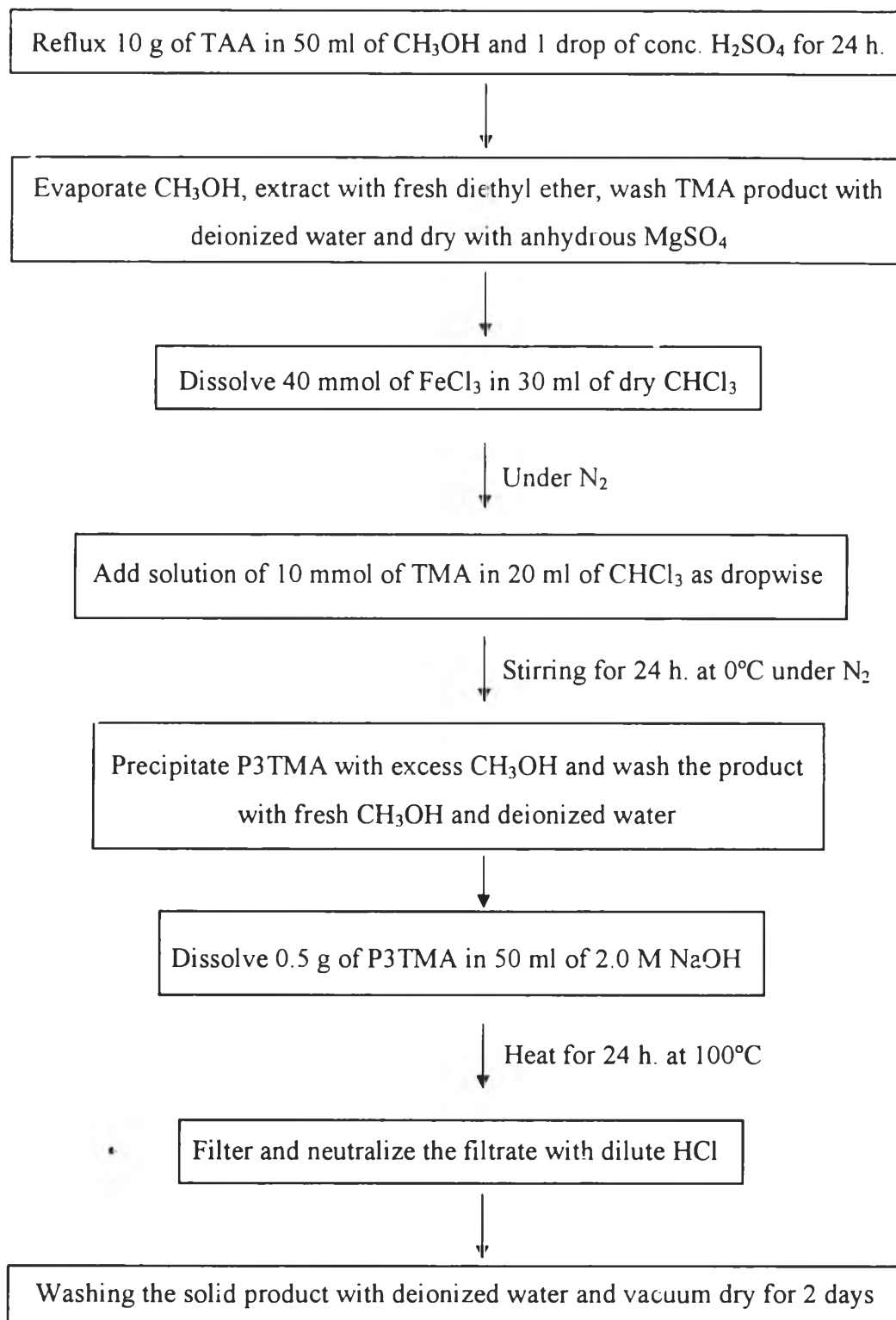


Figure 3.1 Synthesis route of poly(3-thiophene acetic acid).

3.2.2 Doping of Polythiophene

To examine the effect of particle conductivity on the electrorheological properties, P3TAA had different conductivity values were prepared by doping with perchloric acid (Kim *et al.*, 2000). The 2.0 M HClO₄ doped P3TAA was prepared by immersing P3TAA particles in 2.0 M HClO₄ solution at room temperature for 3 days. The doping level was varied by varying the mole ratio of dopant to the monomer, HClO₄/P3TAA (doping ratio equal 1:1, 10:1 and 200:1). After the doping process, their electrical conductivity was studied by using custom-built two-point probe electrometer (Keithley, Model 6517A).

3.2.3 Preparation of Pure Polyisoprene

The electrorheological properties of pure polyisoprene were investigated in terms of electric field strength and crosslinking ratio. To study the effect of crosslinking, an appropriate amount of dicumyl peroxide was mixed with polyisoprene and cast on a mold (diameter 25 mm). We removed bubbles in a vacuum atmosphere at 25°C for 2 h. Various amounts of dicumyl peroxide were used to vary the degree of crosslinking (crosslinking ratios, 2, 3, 5 and 7). The fabrication of the crosslinked polyisoprenes was by compression molding at 175°C and 5 MPa for 7 min (Faez *et al.*, 1999).

3.2.4 Preparation of the P3TAA/Polyisoprene Blends

The polythiophene powder was sieved with a mesh particle size of 38 μm and dried at room temperature for 24 hours prior to their uses. The blends were prepared by mechanical blending of doped and undoped synthesized polythiophene particles, at various particle concentrations (5, 10, 20, and 30%vol.) with polyisoprene. We removed bubbles in a vacuum atmosphere at 25°C for 2 h. The optimum degree of crosslinking, having the highest rheological sensitivity, was used. (crosslinking ratio of about 3). The fabrication of the P3TAA/crosslinked polyisoprene blends was by compression molding at 175°C and 5 MPa for 7 min (Faez *et al.*, 1999).

3.2.5 Characterization and Testing

3.2.5.1 *Fourier-Transform Infrared Spectrometer (FT-IR)*

Each undoped and doped poly(3-thiophene acetic acid) samples was identified for functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavenumber range of $4000\text{-}400 \text{ cm}^{-1}$ using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized P3TAA was intimately mixed with dried KBr at a ratio of P3TAA:KBr = 1:20. Samples were grounded with a mortar, mixed with KBr and molded into pellets under the pressure of 8 tons.

3.2.5.2 *UV-Visible Spectroscopy*

UV-Vis spectra were recorded with a UV-Vis absorption spectrometer (Perkin-Elmer, Lambda 10). Measurements were taken in the absorbance mode in the wavelength range of 200-800 nm. Synthesized P3TAA and doped P3TAA were grinded into a fine powder, dissolved in DMSO at the concentration of $6.0 \times 10^{-5} \text{ M}$ and pipetted into the sample holder. Scan speed was 240 mm/min, and a slit width of 2.0 nm using a deuterium lamp as the light source.

3.2.5.3 *Thermogravimetric Analysis (TGA)*

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to determine amount of moisture content and dopant, and decomposition temperature of undoped and doped poly(3-thiophene acetic acid) (P3TAA) at various mole ratios of dopant, crosslinked polyisoprene (PI_03) and polythiophene/polyisoprene blends (Pth_U/PI_03) with the temperature scan from 30 to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$. The samples were weighted in the range of 5-10 mg and loaded into a platinum pan, and then heated it under an oxygen gas flow.

3.2.5.4 *Scanning Electron Microscope (SEM)*

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology and surface appearance of poly(3-thiophene acetic acid) in powder forms and to identify morphology of undoped polythiophene/polyisoprene blend films at various particle concentrations. A piece of sample was placed on the holder with an adhesive carbon

tape and coated with a layer of gold by using JFC-1100E ion-sputtering device for 4 seconds before measurements were taken. The scanning electron micrographs of polythiophene powder and polymer blends were obtained by using an acceleration voltage of 20 kV with a magnification of 1,500 and 350 times.

3.2.5.5 Particle Size Analyzer

The particle sizes of poly(3-thiophene acetic acid) were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lenses used in this experiment were 45 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

3.2.5.6 Conductivity Measurement: Two-Point Probe Meter

Electrical conductivity is the inversion of specific resistivity (ρ) which indicates the ability of material to transport electrical charge. The meter consists of two probes, making contact on a surface of film sample. These probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage was plotted versus the current change to determine the linear ohmic regime of each sample. The applied voltage and the current change in the linear ohmic regime were converted to the electrical conductivity of polymer using equation (3.1) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (3.1)$$

Where σ is specific conductivity (S/cm), ρ is specific resistivity ($\Omega \cdot \text{cm}$), R_s is sheet resistivity (Ω), I is measure current (A), K is geometric correction factor, V is applied voltage (voltage drop) (V), and t is pellet thickness (cm).

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known;

we used silicon wafer chips (SiO₂). In our case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated by equation (3.2) as follow:

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (3.2)$$

Where K is geometric correction factor, ρ is known resistivity of standard silicon wafer ($\Omega \cdot \text{cm}$), t is film thickness (cm), R is film resistance (Ω), and I is measure current (A).

3.2.5.7 Crosslink Density Determination

The crosslink density can be determined by measurement of M_c the so called equilibrium swelling. We can determine M_c by knowing the swelling ability of certain solvents in a crosslinked network. The procedure of the crosslink density measurement was as follow; initially the samples were cut to a dimension of $\approx 10 \times 10$ mm. Weight of each specimen was then measured. Then we placed each specimen in a vial containing toluene for 3 days and the weight of the swollen sample was measured again. The crosslink density was calculated from the equations (3.3-3.7) (Painter *et al.*, 1997; Choi, 1999; Boochathum *et al.*, 2001). Experiment of each crosslinking ratio was carried out using three samples and data were averaged.

$$M_c = \frac{v_1 \rho_2 \left(v_{2m}^{1/3} - \frac{v_{2m}}{2} \right)}{- \left[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 \right]} \quad (3.3)$$

$$v_{2m} = \frac{w_0}{v_{equil} \times \rho_2} \quad (3.4)$$

$$v_{equil} = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \quad (3.5)$$

$$\chi = 0.34 + \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \quad (3.6)$$

and

$$\text{Crosslink density} = [2M_c]^{-1} \quad (3.7)$$

Where v_1 is the molar volume of solvent, M_w /density, ρ_2 is polymer density, polyisoprene $\approx 0.92 \text{ g/cm}^3$, ρ_1 is solvent density, toluene $\approx 0.867 \text{ g/cm}^3$, w_0 is original polymer weight, w_s is swollen polymer weight, χ is polymer-solvent interaction parameter, R is Gas constant, 8.29 N.m/mol.K , T is temperature 298 K , δ_1 is solubility parameter of polymer, polyisoprene $\approx 17.02 \text{ (MPa)}^{1/2}$, and δ_2 is solubility parameter of solvent, toluene $\approx 18.20 \text{ (MPa)}^{1/2}$.

3.2.5.8 *Electrorheological Properties Measurement*

A melt rheometer (Rheometric Scientific, ARES) was used to measure rheological properties. It is fitted with a custom-built copper parallel plates fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek, GFG 8216A), which can deliver electric field strength to 2 kV/mm . A digital multimeter was used to monitor voltage input. In these experiments, the oscillatory shear strain was applied and the dynamic moduli (G' and G'') were measured as functions of frequency and electric field strength. Strain sweep tests were first carried out to determine the suitable strain to measure G' and G'' in the linear viscoelastic regime. The appropriate strain was determined to be 220% for pure polyisoprene fluid and doped polythiophene suspend in polyisoprene fluid (doping ratio 1:1, 10:1 and 200:1). For the crosslinked polyisoprene (PI_02, PI_03, PI_05 and PI_07) and undoped polythiophene/crosslinked polyisoprene blends (blends ratio 5, 10, 20, and 30%vol.) the appropriate strain was 1%. Then frequency sweep tests were carried out to measure G' and G'' of each sample as functions of frequency. The deformation frequency was varied from 0.1 to 100 rad/s. Prior to each measurement, each polyisoprene and polythiophene/polyisoprene blends samples were presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 10 minutes to ensure the formation of equilibrium polarization before each measurement was taken. Each measurement was carried out at the temperature of 27°C and repeated at least two or three times.