



CHAPTER III EXPERIMENTAL

3.1 Materials

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer and anhydrous ferric chloride, FeCl_3 (AR grade) was used as the oxidant as received. Chloroform, CHCl_3 (AR grade, Lab-Scan), methanol, CH_3OH (AR grade, Lab-Scan), and dimethyl sulfoxide, DMSO (AR grade, Lab-Scan) were dried over CaH_2 for 24 h under the nitrogen atmosphere and then distilled, prior to be used as solvents. Hydrochloric acid, HCl (AR grade, Lab-Scan) was used to neutralize and to precipitate the polymer synthesized. Sulfuric acid, H_2SO_4 was used to protect the oxidative decomposition of the monomer. Diethyl ether, $\text{C}_4\text{H}_{10}\text{O}$ and distilled water were used to extract and to wash materials. Sodium hydroxide, NaOH was used as the hydrolyzing agent. Perchloric acid, HClO_4 , (AR grade, Panreac Quimica) was used as received as the dopant.

Zeolite Y with different Si/Al ratios were purchased from Zeolyst International (USA).

Nitrogen (99 %, TIG) was used as the carrier gas of ammonia (99.99 %, Poontaweporn Limited Partnership) was used to investigate the electrical conductivity responses of the composites.

3.2 Equipment

A FT-IR spectrometer (Thermo Nicolet, Nexus 670), with 32 scans, a resolution of $\pm 4 \text{ cm}^{-1}$, and covering a wavenumber range of 4000-400 cm^{-1} , was used to investigate spectra of poly(3-thiophenemethyl acetate) (P3TMA), undoped and doped poly(3-thiophene acetic acid) (Pth). The interaction of the active sites of Pth_10:1 and zeolite NaY with NH_3 were investigated by FTIR spectroscopy. A thermal gravimetric analyzer (Perkin Elmer) was used to characterize the thermal property of undoped and doped poly(3-thiopheneacetic acid) (Pth) at 10:1 mole ratio

of dopant to monomer unit. Measurements were carried out with the temperature scan from 30 to 800 °C and a heating rate of 10 °C/min. A Particle size analyser (Malvern, Mastersizer X Version 2.15) was used to measure the particle size of undoped and doped poly(3-thiophene acetic acid). A X-ray Diffractometer (XRD) (D/MAX 2200) was used to identify crystallinity and structures of poly(3-thiopheneacetic acid) and zeolite. A pycnometer was used to measure the specific density (ρ_p) of the conductive polymer and zeolite. A custom-built two-point probe (Keithley, Model 6517A) was used to measure the electrical conductivity of Pth and its composites. Morphology of undoped and doped poly(3-thiopheneacetic acid), zeolites, and composites were examined by scanning electron microscopy (SEM). A surface area analyzer (Physisorption) (Quantachrome, Autosorb-1MP) was used to measure the surface area and the pore size of zeolites Y.

3.3 Methodology

3.3.1 Synthesis of Poly(3-thiopheneacetic acid) (Pth) (Kim *et al.*, 1999)

3.3.1.1 *Preparation of Monomer*

Poly(3-thiopheneacetic acid) was prepared by a reflux 10.0 g of 3-thiopheneacetic acid (3TAA) in 50 ml of dry methanol with 1 drop of concentrated H₂SO₄ for 24 h. Then, methanol was evaporated and the residue was extracted with diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO₄, and filtered. The 3-thiophene methyl acetate (3TMA) was recovered after diethyl ether was evaporated.

3.3.1.2 *Preparation of Poly(3-thiopheneacetic acid)*

The prepared monomer, 3-thiophene methyl acetate(3TMA), of 10 mmol was dissolved in 20 ml chloroform and then added dropwise to a solution of 40 mmol ferric chloride in 30 ml chloroform under nitrogen atmosphere. The reaction was carefully maintained at 0 ± 0.5 °C for 24 h. The mixture was precipitated by pouring the solution in an excess amount of methanol. Then the precipitate was washed with methanol and distilled water. Finally, poly(3-thiophenemethyl acetate)(P3TMA) was obtained.

P3TMA was hydrolyzed by heating 0.5 g precipitate in 50 ml of 2.0 M NaOH solution for 24 h at 100 °C. Poly(3-thiopheneacetic acid) (Pth) was obtained by neutralization and precipitation in a dilute HCl solution. Pth was repeatedly washed with distilled water before vacuum drying at room temperature for 2 days.

3.3.2 Preparation of Doped Poly(3-thiopheneacetic acid)

Pth particles was stirred in 2.0 M HClO₄ at room temperature for 3 days. The doping ratio of HClO₄/3TAA were varied from 1:1 to 300:1. Doped Pth was filtered and vacuum-dried (Thuwachaowsoan *et al.*, 2007).

3.3.3 Preparation of the Pth/Zeolite Composites

Before mechanical mixing, poly(3-thiopheneacetic acid) was grinded and sieved with mesh size of 38 µm. Then, zeolite was grinded and dried before mixing with Pth grinding. After mixing, the composites were pressed into a pellet form by a hydraulic press machine.

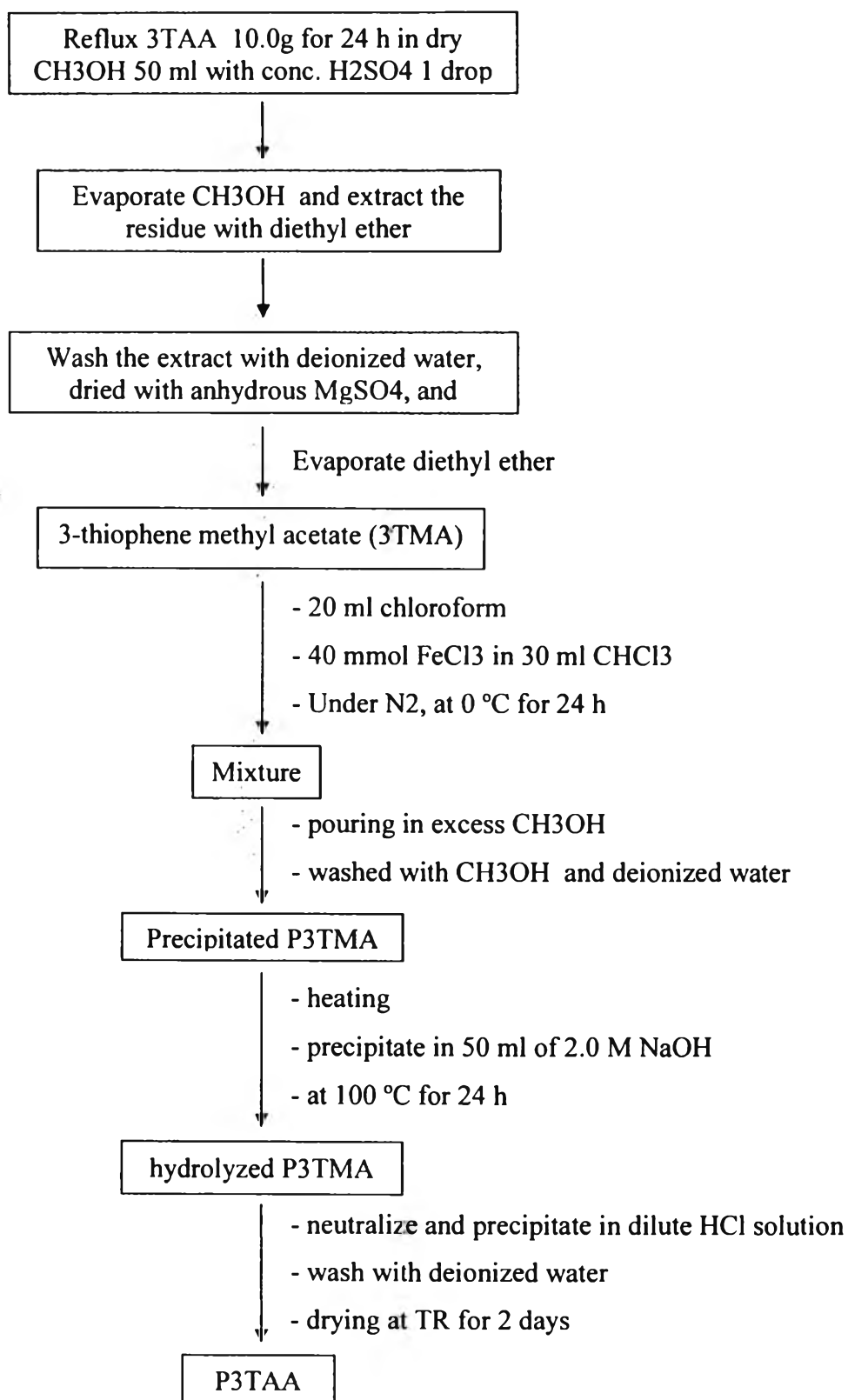


Figure 3.1 Preparation of the poly(3-thiopheneacetic acid) (Pth) flow diagram.

3.3.4 Characterization

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

Undoped and doped poly(3-thiophene acetic acid) (Pth) powders were investigated for their functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of ± 4 cm⁻¹, covering a wavenumber range of 4000-400 cm⁻¹. Optical grade KBr was used as the background material and the polymers were mixed with dried KBr at a ratio 1:20. In order to investigate the spectrum of Pth_{10:1} and zeolites Y, before exposure, under exposure, and after exposure with NH₃ gas, a gas cell with ZnSe window was used.

3.3.4.2 *Thermogravimetric Analyzer (TGA)*

A thermal gravimetric analyzer (Perkin Elmer) was used to characterize the thermal property of the undoped and the doped poly(3-thiopheneacetic acid) (Pth) at 10:1 mole ratio of dopant to monomer unit. Measurements were carried out with the temperature scan from 30 to 800 °C and a heating rate of 10 °C/min. The samples were weighed in the range of 5-20 mg and loaded into a platinum pan, and then it was heated under N₂ flow.

3.3.4.3 *Particle Size Analyzer*

The average particle size of poly(3-thiophene acetic acid) and the zeolites were determined by a particle size analyzer (Malvern, Mastersizer X Version 2.15). The samples were grounded and sieved with mesh size 38 μ m before measurements were taken.

3.3.4.4 *X-ray Diffractometer (XRD)*

A X-ray Diffractometer (XRD) (D/MAX 2200) was used to identify the crystallinity and the structure of poly(3-thiopheneacetic acid) and the zeolites. Powders of the polymer and the zeolites were packed onto a glass plate and data were collected after X-ray passed through the sample.

3.3.4.5 *Scanning Electron Microscope (SEM)*

Morphology of undoped and doped poly(3-thiopheneacetic acid), the zeolites, and the composites were observed by the scanning electron

microscopy (SEM)(JEOL, JSM-5410LV). Sample was coated with gold for improving conductivity.

3.3.4.6 BET

Surface area and pore size of zeolites Y were measured by using a surface area analyzer (Physisorption) (Quantachrome, Autosorb-1MP). Zeolite powder was weighed and out gassed at 300 °C over night before the adsorption and the desorption with He and N₂ gases. During the operation, the zeolite powder was cooling by liquid N₂.

3.3.4.7 Two-Point Probe Meter

A custom-built two-point probe with a linear geometric array (Keithley, Model 6517A) was used to measure the specific conductivity of each sample. Current used was in the linear Ohmic regime.

3.3.5 Electrical Conductivity Measurement

The specific electrical conductivity values, σ (S/cm), of the poly(3-thiopheneacetic acid) and the composites were measured by using a custom-built two-point probe. The specific electrical conductivity was calculated from:

$$\sigma = (1/Rt)(1/K) \quad (1)$$

where t is the pellet thickness, and K is the geometric correction factor which is equal to the ratio w/l , where w and l are the width and the length of probe, respectively. The value of K was determined by calibrating the two-point probe with semi-conducting silicon sheet of known resistivity value.

A custom-built two-point probe consist of two chambers of equal volume. All measurements were taken at 26 ± 1 °C and 1.1 atm in the linear Ohmic regime. The procedures for measuring the electrical conductivity in the presence of ammonia (NH₃) gas were as follows.

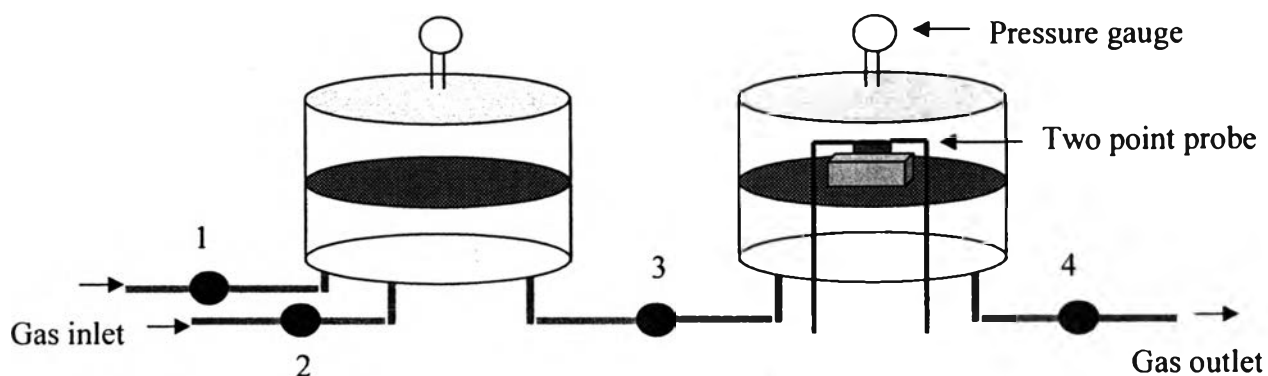


Fig 3.2 Conductivity detectors with gas chamber.

The procedure was as follows.

Step 1 The sample was measured the specific electrical conductivity in air.

Step 2 The chambers were evacuated of air and moisture by using a vacuum pump (valve No. 1 and 2 were closed; valve No. 3 and 4 were open) and the steady state electrical conductivity value in vacuum was measured.

Step 3 Valve no.3 and valve no. 4 were closed.

Step 4 Nitrogen gas was injected until the pressure reached 1.2 atm, to prevent leakage, (valve no.3 was open) and the steady state electrical conductivity value was measured as $\sigma_{N_2 \text{ initial}}$.

Step 5 The chambers were re-evacuated.

Step 6 Ammonia gas was injected until the pressure reached 1.1 atm and (valve no.3 was open) the steady state electrical conductivity (σ_{NH_3}) was measured.

Step 7 Ammonia gas was evacuated

Step 8 Nitrogen gas was injected until the pressure reached 1.2 atm, to prevent leakage, (valve no.3 was open) and the steady state electrical conductivity value was measured as $\sigma_{N_2 \text{ final}}$.

From the procedure of measurement, the electrical conductivity response can be calculated from;

$$\Delta\sigma = \sigma_{NH_3} - \sigma_{N_2 \text{ initial}} \quad (2)$$

and the sensitivity ($\Delta\sigma/\sigma_{N_z \text{ initial}}$) of poly(3-thiopheneacetic acid) and composites were recorded.