



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

$\alpha,\alpha'$ -dichloro-p-xylene, tetrahydrothiophene and methanol are purchased from the Aldrich Company was used to synthesize p-xylene-bis(tetrahydrothiophenium chloride)monomer. Sodium hydroxide (Merck) and Hydrochloric acid (Merck) were used as a basic and acid reagent, respectively. Sulfuric acid (Merck) was used as an oxidant.

Zeolite: CVB100 (Si/Al = 5.1,  $\text{NH}_3^+$ ) (Zeolyst), CVB300 (Si/Al = 5.1,  $\text{Na}^+$ ) (Zeolyst), CVB400 (Si/Al = 5.1,  $\text{H}^+$ ) (Zeolyst), CVB720 (Si/Al = 30,  $\text{H}^+$ ) (Zeolyst), CVB760 (Si/Al = 60,  $\text{H}^+$ ) (Zeolyst), CVB780 (Si/Al = 80,  $\text{H}^+$ ) (Zeolyst) were used as the adsorbents. All chemicals were used without further purification.

Ammonium Nitrate ( $\text{NH}_4\text{NO}_3$ ) was used as the target gas. Nitrogen ( $\text{N}_2$ , TIG) was used as the surface cleaning gas.

### 3.2 Equipments

A FT-IR Spectrometer, (Nicolet, Nexus 670), with 32 scans and  $\pm 4$   $\text{cm}^{-1}$  resolution, was used to identify functional groups of synthesized PPV and doped PPV. A Thermal Gravimetric Analyzer (duPont, TGA 2950) was used to study thermal property of PPV under air atmosphere with heating rate of 10  $^\circ\text{C}/\text{min}$  and temperature scan from 30-600  $^\circ\text{C}$ . An X-ray Diffraction Microscope, (Phillips, Rigaku) was utilized to observe the crystallinity of materials. The morphology of materials was observed by using a Scanning Electron Microscope, (JEOL, JSM 5200) and their particle size diameter were determined by using a Particle Size Analyzer, (Malvern, Mastersizer X Version 2.15). A Surface Area Analyzer (Quantachrome, Autosorb-1) was used to examine the surface area and total pore volume of zeolite. The electrical conductivity of PPV and its composites was measured by using a custom-built two-point probe meter, (Keithley, Model 6517A).

### 3.3 Methodology

#### 3.3.1 Poly(*p*-phenylene vinylene) (PPV) Synthesis and Doping Process

##### *3.3.1.1 Preparation of monomer*

Synthesis of the *p*-xylene-bis(tetrahydrothiophenium chloride) monomer was achieved by reacting  $\alpha,\alpha'$ -dichloro-*p*-xylene at a concentration of 0.75 M with excess tetrahydrothiophene at 50 °C in methanol: water (80:20) solution for 24 h. This monomer was purified concentrating the reaction solution and precipitating the product in cold acetone (0 °C), filtration and vacuum drying.

##### *3.3.1.2 Preparation of precursor sulfonium polyelectrolyte*

The precursor sulfonium polyelectrolyte was prepared in aqueous solution by the base induced polymerization of an appropriate *bis*-sulfonium monomer. The reaction was usually carried out at low temperatures in fairly dilute monomer solutions and in equimolar base to monomer ratios in order to suppress the premature formation of unsaturated polymer segments by thermal or base induced elimination of solubilizing side chains. The polymerization reaction was terminated by the addition of dilute aqueous hydrochloric acid to the reaction mixture which was then dialysed against water in order to separate the high molecular weight fraction from the monomeric and oligomeric residues as well as the sodium and chloride ions.

##### *3.3.1.3 Preparation of Poly(*p*-phenylene vinylene)*

Poly(*p*-xylene-bis(tetrahydrothiophenium chloride)) films were heated under vacuum at 180 °C for 6 hr.

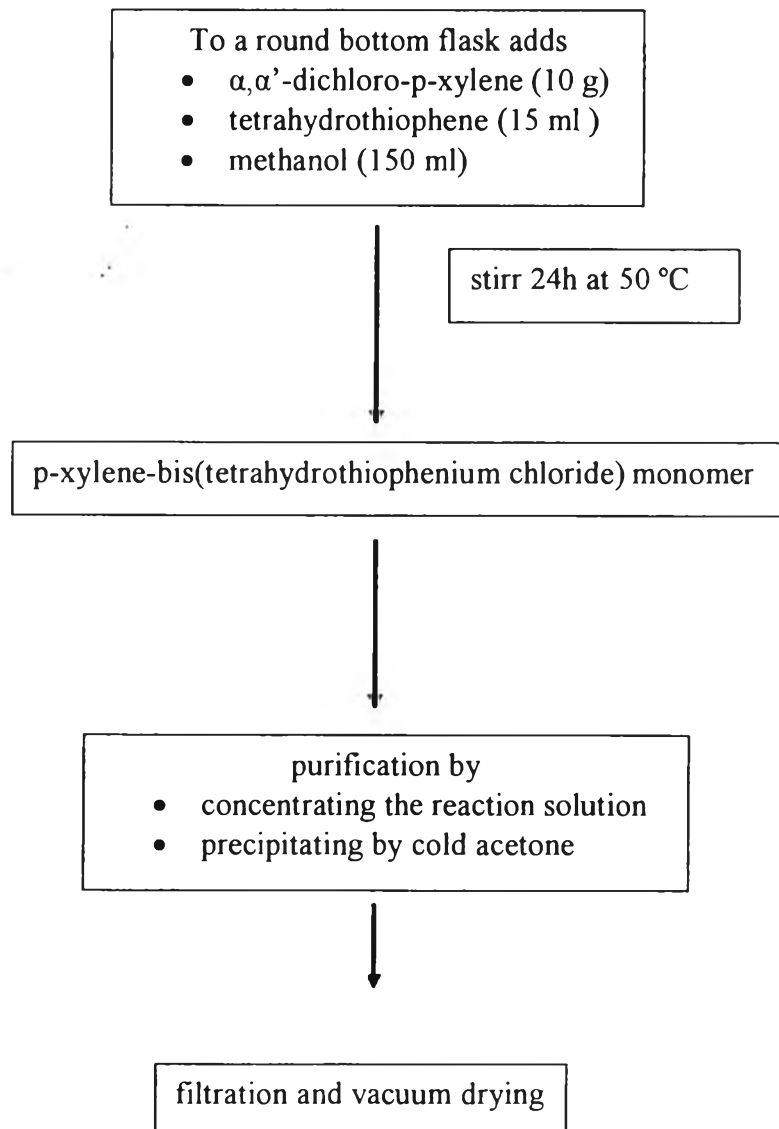
##### *3.3.1.2 Poly(*p*-phenylene vinylene) Doping*

The 18 M Sulfuric acid was used as dopant solution at mole ratios between the PPV repeating unit per sulfuric acid equal to 1:1, 1:50, 1:100, 1:200, 1:300. The doping process occurred after adding a dopant solution to a polymeric powder and it was monitored by observing the colour changes of powder from bright yellow to black.

### 3.3.2 Composite Preparation

Dried PPV powder was sieved with 53  $\mu\text{m}$  sieve prior to being mechanically mixed with Zeolite Y at %volume of zeolite equal to 90. The composites were compressed into a disc form by using a hydraulic press at pressure equal to 6 tons and the conductivity values were measured by using the two-point probe technique.

#### Preparation of monomer



**Preparation of Poly(p-xylene-bis(tetrahydrothiophenium chloride))**

To a round bottom flask

- p-xylene-bis(tetrahydrothiophenium chloride) monomer
- 0.4 M NaOH

↓

Stir under N<sub>2</sub> flow at 0 °C, 120 min

↓

Stop the reaction with 0.4 M HCl

↓

Dialysis in CH<sub>3</sub>OH/H<sub>2</sub>O (1:1 by volume) for 3 days

**Preparation of Poly(p-phenylene vinylene) :PPV**

Poly(p-xylene-bis(tetrahydrothiophenium chloride))

↓

Heat under vacuum at 180 °C, 6hr

↓

Poly(p-phenylene vinylene)

### 3.3.3 Characterization

#### *3.3.3.1 Fourier-Transform Infrared Spectrometer (FT-IR)*

Each PPV sample was identified for its functional groups by a FT-IR spectrometer (Bruker, FRA 106/S) in the absorption mode with 32 scans at a resolution of  $4\text{ cm}^{-1}$ . Samples were grounded with a mortar, mixed with KBr and molded into pellets under the pressure of 8 tons. The observed spectra were in the range of 400-4000 nm.

#### *3.3.3.2 Thermogravimetric Analyzer (TGA)*

The moisture content and degradation process of undoped poly(p-phenylene vinylene), doped poly(p-phenylene vinylene), zeolite and polyaniline/zeolite composite were determined by a thermalgravimetric analyzer (Dupont, TGA 2950). Sample powder was weighted at 10-15 mg and put in a titanium pan. The instrument was operated from 30 to 900 °C with a heating rate of 10°C/min.

#### *3.3.3.4 X-ray Diffractometer (XRD)*

The crystallinity of poly(p-phenylene vinylene) and the crystal order of zeolite were determined by an X-ray diffractometer (Phillips PW 1830/00 No. DY1241 Diffractometer, model Rigaku). A pellet form of poly(p-phenylene vinylene) sample was placed on quartz specimen. X-ray diffraction patterns were started from  $2\theta = 5$  to 90 degrees.

The crystal structure of the zeolites was also determined by grinding sample with a mortar and placing it on a glass specimen. X-ray pattern of Zeolite was observed at  $2\theta$  equal to 5 to 90 degrees.

#### *3.3.3.5 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(p-phenylene vinylene) in powder and to identify morphology of zeolite powder. A piece of sample was placed on the holder with an adhesive tape and coated with a layer of gold by using a JFC-1100E ion-sputtering device before measurements taken. The scanning electron micrographs of poly(p-phenylene vinylene) were obtained by using an acceleration voltage of 25 kV with a magnification of 1000-3500 times.

### 3.3.3.6 Particle Size Analyzer

The particle sizes of poly(p-phenylene vinylene) and zeolite samples were determined by using a particle size analyzer, (Malvern Instruments Ltd. Masterizer X Version 2.15). The lenses used in this experiment were 45 and 300 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the size distribution. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

### 3.3.3.7 BET

BET (Quantachrome, Autosorb-1) was used to measure the pore size and surface area of each zeolite. Zeolite powder was weighted 0.1-0.5 mg and outgassed at 300 °C before each measurement.

### 3.3.3.8 Conductivity Measurement: Two-Point Probe Meter

Electrical conductivity is the inversion of specific resistivity ( $\rho$ ) which indicates the ability of material to transport electrical charge. The meter consists of two probes, making contact on a surface of film sample. One probe were connected to a voltmeter for recording a change in voltage, while the another probe is connected to a constant current source. The voltage change was converted to the electrical conductivity of polymer using equation (3.1) as follow:

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

where  $\sigma$  is specific conductivity (S/cm),  $\rho$  is specific resistivity ( $\Omega \cdot \text{cm}$ ),  $R_s$  is sheet resistance ( $\Omega/\text{sq}$ ),  $t$  is thickness of sample pellet (cm),  $V$  is applied voltage (voltage drop) (V),  $I$  is measured current (A), and  $K$  is geometric correction factor of the two-point probe meter.

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. In our case,

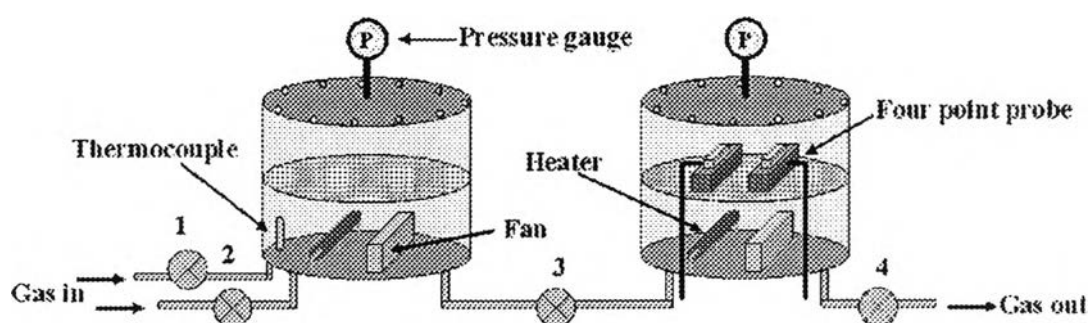
the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was computed by equation (3.2) as follows:

$$K = \frac{\rho_{ref}}{R_s \times t} \quad (3.2)$$

Where  $\rho_{ref}$  is the known resistivity calibrated from the 4-point probe device ( $\Omega \cdot \text{cm}$ ) and  $t$  is the film thickness (cm).

### 3.3.5 Gas measurement

Measurements of conductivity responses of PPV, dPPV and dPPV/Zeolite Y composites were recorded by using a specially constructed gas cell. It consisted of two chambers connected in series. The chambers were made from stainless steel No.304. The second chamber contained two point probe meters for conductivity measurement. The temperature controllers, connecting to both chambers, were used to monitor and control the temperature within the gas chambers.



**Figure 3.1** Conductivity detectors with gas chamber.

**Step 1** A voltage was applied to PPV pellets in order to measure conductivity before exposing to gas.

**Step 2** Both chambers were closed and evacuated by using a vacuum pump in order to remove gases (valve No. 1 and 2 was closed; valve No. 3 and 4 was opened).

**Step 3** Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) was closed.

**Step 4** N<sub>2</sub> gas was fed into the first chamber until the pressure reaches 1 atm as observed from the pressure gauge.

**Step 5** Valve No. 3 was opened; the conductivity response of N<sub>2</sub> gas was recorded.

**Step 6** Steps 2-6 was repeated until the conductivity response of N<sub>2</sub> was constant (this refers to pre-exposed  $\sigma_{N_2, initial}$ ).

**Step 7** Both chambers were closed and evacuated by using a vacuum pump in order to remove gases.

**Step 8** Ammonium nitrate vapor will be fed into the first chamber until the pressure reached 0.1 atm as observed from the pressure gauge and N<sub>2</sub> was then fed to mix with previous fed NH<sub>4</sub>NO<sub>3</sub> until pressure reached 1 atm observed from pressure gauge. The obtained ammonium nitrate concentration was 0.377% by volume.

**Step 9** Valve No. 3 was opened; the conductivity response of NH<sub>4</sub>NO<sub>3</sub>-N<sub>2</sub> mixture gas was recorded until it reaches an equilibrium value.

**Step 10** Both chambers was closed and evacuated by using a vacuum pump in order to remove gas.

**Step 11** Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) was closed.

**Step 12** N<sub>2</sub> gas was fed into the first chamber until the pressure reaches 1 atm as observed from the pressure gauge.

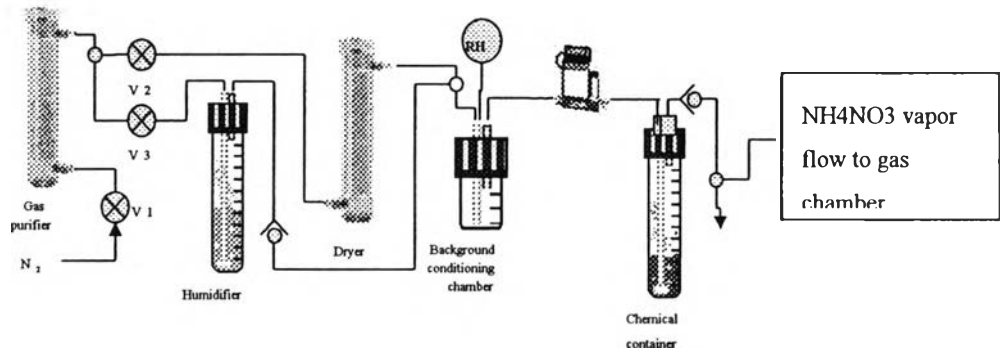
**Step 13** Valve No. 3 was opened then the conductivity response of N<sub>2</sub> gas will be recorded as the final  $\sigma_{N_2, final}$ .

The differences in the change of electrical conductivity ( $\Delta\sigma$ ) at various doping ratios were calculated by Equation (3.4) following;

$$\Delta\sigma = \sigma_{NH_4NO_3} - \sigma_{N_2, final} \quad (3.3)$$



Where  $\Delta\sigma$  is the difference in specific conductivity (S/cm),  $\sigma_{N_2, \text{final}}$  is the specific conductivity of  $N_2$  at final (S/cm) and  $\sigma_{NH_4NO_3}$  is the specific conductivity of  $NH_4NO_3$  (S/cm).



**Figure 3.2** Flow system unit.

Ammonium nitrate vapor was prepared by Flow system unit (Fig 3.2).  $N_2$  was flowed to the chemical chamber. The flow rate of  $N_2$  is 5 L/min. After that, there was the evaporation of Ammonium Nitrate vapor.

The flow rate of  $NH_4NO_3$  was measured by the slope of calibration curve between volume of  $NH_4NO_3$  (L) and the elapsed time (min). The flow rate of  $N_2$  from the flow controller was 5 L/min.  $N_2$  was flown through the chemical solution chamber to form a vapor. The vapor concentration was calculated from volume flow rate of  $NH_4NO_3$  (L/min) divided by total volume flow rate ( $V_{N_2} + V_{NH_4NO_3} + V_{H_2O}$ , L/min) as:

$$\% \text{ Vapor concentration} = \left( \frac{V_{NH_4NO_3}}{V_{N_2} + V_{NH_4NO_3} + V_{H_2O}} \right) \times 100 \quad (3.4)$$

Where  $V_{NH_4NO_3}$  is volume flow rate of  $NH_4NO_3$  (L/min),  $V_{N_2}$  is volume flow rate of  $N_2$  (L/min) and  $V_{H_2O}$  is volume flow rate of  $H_2O$  (L/min).