

## CHAPTER III EXPERIMENTAL

### 3.1 Materials.

Analytical grade aniline monomer (Merck) was used as a monomer. Analytical grade ammonium peroxydisulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Merck) was used as an oxidant. Twenty five percent of analytical grade ammonia solution,  $(\text{NH}_3.\text{H}_2\text{O})$  (Merck) was used as a base reagent. Analytical grade calcium hydride,  $(\text{CaH}_2)$  (Fluka) was used in drying the aniline monomer. Thirty eight percent of analytical grade hydrochloric acid,  $(\text{HCl})$  (Merck) was used as acid medium in the synthesis process. Purum 99% camphor-10-sulfonic acid (Fluka), forty eight percent of analytical grade hydrogen bromide,  $(\text{HBr})$  (Univar), and ninety eight percent of analytical grade maleic acid (Fluka) were used as protonic acid in doping process. Analytical grade 1-methyl-2-pyrrolidone (NMP) (Merck) was used as a solvent in the UV-Visible spectroscopy measurement. Analytical grade methanol,  $(\text{CH}_3\text{OH})$  (LAB-SCAN) was used in washing excess acid in the polyaniline synthesis process. Nitrogen gas ( $\text{N}_2$ ), of UHP grade with 99% purity, (TIG) was used as a carrier gas. The 1000-ppm carbon monoxide ( $\text{CO}$ ) balanced with nitrogen (TIG) was used as a target gas.

### 3.2 Methodology.

#### 3.2.1 Purification of Aniline Monomer.

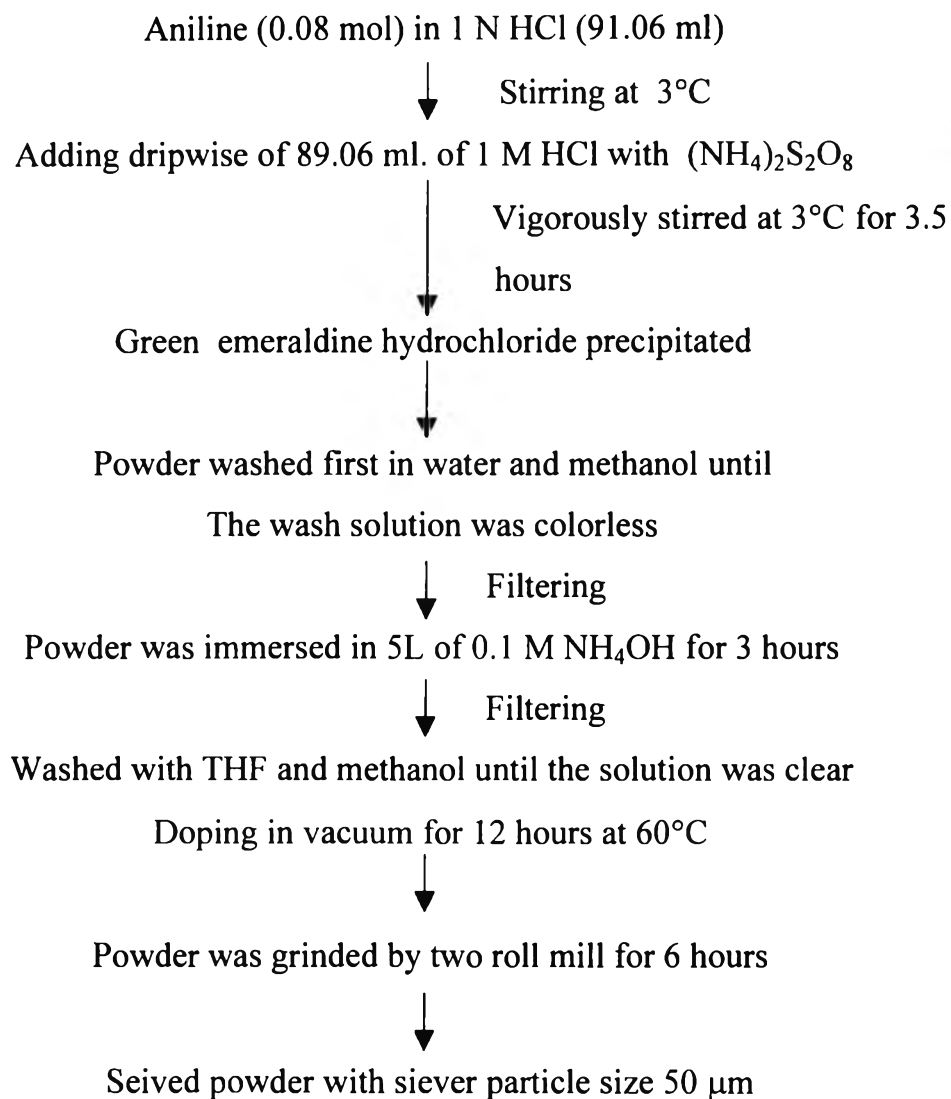
Aniline monomer was distilled by the method of Perrin (1985). 100 ml of aniline monomer was dried with 0.25 grams of calcium hydride  $(\text{CaH}_2)$  for 30 minutes. The dried aniline was twice distilled under reduced

pressure at 50-60°C. Colorless aniline monomers were obtained and stored in nitrogen atmosphere at 0°C prior to use.

### 3.2.2 Synthesis of Polyaniline Base.

A solution of 1 N HCl was prepared by adding 98.54 mL of thirty eight percent of HCl and 901.46 mL of distilled deionized water in a volumetric flask. Then 89.06 mL of this acid solution was placed into a polymerization vessel along with 7.669 g (0.08 mol) of distilled aniline and the mixture was stirred at 0°C. In a separate flask, 98.44 mL of 1 M HCl was combined with 14.6779 g (0.06 mol) of ammonium peroxodisulfate. This mixture was stirred until all of the oxidant dissolved and then cooled to 0°C. Thereafter, the persulfate solution was dropwise added to the aniline solution within a period of one hour. The combined solution was allowed to react for 3.5 hours at -5 to 0°C. The green emeraldine hydrochloride precipitate was collected by large Buchner funnel. The powder was extracted first in water and then methanol until the wash solutions were colorless and finally filtered. The powder of polyemeraldine hydrochloride salt was subsequently immersed in 312.5 mL of 0.1M NH<sub>4</sub>OH for 3 hours, filtered and then washed again with water until the filtrates were neutral. The purified emeraldine base was continually dried in a vacuum at 50°C for 48 hours and then stored in a vacuum desiccator. Emeraldine base was grinded to very small particle by a two roll mill for 6 hours. Finally, the powder was sieved by 50 µm sieve.

### Flow Chart of Chemical Synthesis and Doping Process



### 3.2.3 Preparation of Doped Polyaniline Powder.

#### *3.2.3.1 Hydrogen Bromide Doped Polyaniline (PANI-HCl/HBr).*

A solution of 2M HBr was prepared by adding 253.94 mL forty eight percent of hydrogen bromide and 764.06 mL of distilled deionized water in a 1000 mL volumetric flask. The solution was then stirred for 3 hours at room temperature. Emeraldine base was doped at various mole ratios between an acid dopant and emeraldine base; they were 4, 40, 200, 400, and

1295. Emeraldine base polyaniline powder was weighted at 0.35 g and immersed in the 2M HBr solution at particular volumes of 1.923, 19.23, 96.15, 192.3 and 624.98 mL, respectively. The mixture was then shaken and allowed to reach an equilibrium during a period of 48 hours. The doped powder was filtered and dried at 60°C for 30-40 hours in a vacuum oven.

### *3.2.3.2 Camphor Sulfonic Acid Doped Polyaniline (PANI-HCl/CSA).*

2M CSA solution was prepared by adding 46.46 g of CSA in 100 mL of distilled water. This solution at particular volumes, .96, 1.15, 9.67, 46.2, and 96.68 mL was added into 0.35g polyaniline powder in order to give the ratio of  $N_A/N_{EB}$  of CSA doped polyaniline, 2, 4, 20, 160, and 200, respectively. After that, the mixture was shaken 48 hours. Finally, the doped powder was filtered and dried at 60°C for 30-40 hours in a vacuum oven.

### *3.2.3.3 Maleic Acid Doped Polyaniline (PANI-HCl/MA).*

236.89 g of maleic acid was added into 1000 mL of distilled water in order to prepare a 2M maleic acid solution. In order to obtain maleic acid doped polyaniline at mole ratios, 4, 40, 200, 400, 500, 1000, and 1295, 0.35 g of emeraldine base was immersed in the 2M maleic acid solution at the particular volume of 1.923, 19.23, 96.15, 192.3, 325.5, 425.36, and 624.98 ml, respectively. The mixture was then shaken and allowed to reach an equilibrium during a period of 48 hours. The doped powder was filtered and dried at 60°C for 30-40 hours in a vacuum oven.

### 3.2.4 Preparation of Doped Polyaniline Pellet.

0.06-0.07 g of doped polyaniline powder was pressed into a disc form under the pressure of 3 tons by Graseby specac hydraulic press using a

stainless steel die 2.5 cm. diameter. The pellets, finally, having diameter 2.5 cm and thickness about 0.01-0.02 mm were obtained.

### 3.2.5 Characterization.

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

Infrared spectra were recorded using a FT-IR spectrometer (Bruker, FRA 106/S) in the wavenumber range of 400-40000  $\text{cm}^{-1}$  using the absorbance mode with 64 scans with the wavenumber resolution of  $\pm 4 \text{ cm}^{-1}$ . The KBr technique was used to prepare the powder samples for recording spectrum.

Specimens of the synthesized polyaniline, undoped polyaniline, doped polyaniline and exposed and unexposed polyaniline at each  $N_a/N_{EB}$  ratio were prepared by grinding the powdered polyaniline with the KBr powder. The mixture was molded in special dies under the pressure of 10 tons. The sample spectrum was recorded by using KBr as a background.

FT-IR was used to identify the characteristics functional group of the synthesized polyaniline and the differences in the functional groups between the undoped and doped polyanilines and between the exposed and unexposed polyanilines.

#### *3.2.5.2 UV-Visible Spectrophotometer (UV-Visible).*

UV-Visible spectra were recorded with a UV-Visible spectrometer (Perkin Elmer, Lambda 10). Measurements were taken in the absorbance mode in the wavelength range of 300-900 nm.

Samples were prepared by dissolving in NMP at the concentration of 0.05 g/L and each sample was put in a quartz cell and recorded the UV-visible spectra by using NMP as a background.

UV-Visible spectrophotometer was used to investigate the electronic structure of polyaniline between undoped and doped polyaniline

solution. The absorption spectra of the excitation of benzenoid segments, quinoid segments, bipolaron state, and polaron state were identified.

#### *3.2.5.3 Thermogravimetric Analyzer (TGA).*

Thermal stability, moisture contents, and degradation process of the undoped and doped polyaniline were studied by a thermalgravimetric analyzer (DuPont, model TGA 2950). The samples were weighed at 2-5 mg and put then in a titanium pan. The instrument was set to operate at temperatures from 30 to 700°C at a heating rate of 10°C/min.

#### *3.2.5.4 X-ray Diffraction Analyzer (XRD).*

An X-ray diffractometer (Rigaku model) was used. to investigate orderly arrangements of atoms or molecules and to determine the crystal structures of polymer. X-ray diffraction patterns were recorded on a Phillips PW 1830/00 No. DY 1241 diffractometer. Each XRD sample was the polyaniline powder contained in a glass specimen holder and the diffraction pattern was examined between  $2\theta = 5-60$  degrees.

#### *3.2.5.5 Scanning Electron Microscope (SEM).*

A scanning electron microscope (JOEL, model JSM-5200) was used to identify microstructures of the undoped and doped polyaniline in both of pellet and powder form. SEM digitized photographs were obtained with a magnification range between 35-20,000 times.

The polyaniline pellets were cut into small pieces and adhered on a brass-stub by using an adhesive tape. The samples on stub were coated with thin layer of gold by using a JFC-1100E ion sputtering device. The morphology of polyanilines was obtained by using an acceleration voltage of 25kV with a magnification of 5000 time.

### 3.2.5.6 Particle Size Analyzer.

The particle size of samples was determined by a particle size analyzer, Masterizer X Version. 2.15 (Malvern Instruments Ltd.). The lens used in this experiment was 300 mm and the active beam length was set at 2.40 mm. The sample was placed in a sample cell across a laser beam. This machine analyzed the average particle size and standard size distribution from the laser beam depending on the beam length parameter. Consequently, the specific surface area was calculated from the particle diameter with the assumption of constant volume of spherical particle.

A droplet of surfactants was added in a stirring water chamber in order to help the distribution of polyaniline in water. After that, 0.03 % volume of polyaniline powder was suspended in a stirring water chamber.

### 3.2.6 Conductivity Measurement.

Specific electrical conductivity, the inverse of the specific resistivity, indicates the ability of the charge transfer. This meter consists of four probes, the two of them were connected to a voltmeter for detection of the change in voltage, while the others were connected to a constant current source system. The voltage change was converted to the electrical conductivity of polymer by using Equation (2) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{1}{K \times V_a \times t} \quad (2)$$

where

- $\sigma$  = specific conductivity (S/cm.)
- $\rho$  = specific resistivity ( $\Omega$ .cm.)
- $R_s$  = sheet resistivity ( $\Omega$ )
- $I$  = current (A)
- $K$  = geometric correction factor
- $V$  = voltage drop (V)
- $t$  = pellet thickness (cm).

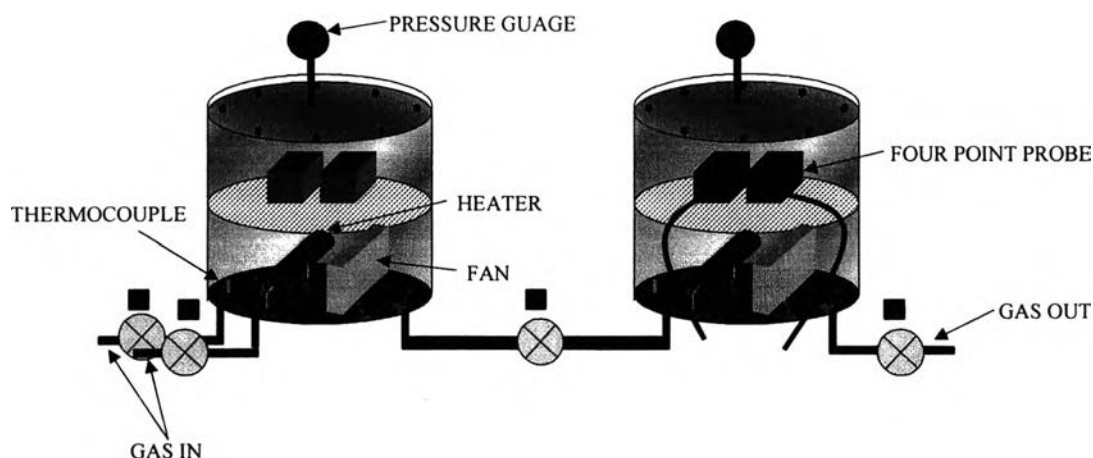
The geometric correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing. The geometric correction determined by using standard materials where specific resistivities were known. In this case, the sheet resistivity was measured by using the four-point probe and then the geometric correction factor was computed by the following Equation:

$$K = \frac{\rho_{\text{ref}}}{R_s \times t} \quad (3)$$

where  $\rho_{\text{ref}}$  = known resistivity from the chemical handbook ( $\Omega \cdot \text{cm}$ )  
 $R_s$  = sheet resistivity ( $\Omega$ )  
 $t$  = film thickness (cm).

Measurements of conductivity responses of doped polyaniline were recorded by using a special constructed gas cell. It consists of two chambers connected in series. The chambers were made from stainless steel No.304. The second chamber contained two four point probe meters for conductivity measurement. The temperature controllers, connecting to both chambers, were used to monitor and control the temperature within the gas chamber.





**Scheme 3.1** A schematic of conductivity detectors with gas chamber.

Step 1 Both chambers were evacuated by using a vacuum pump in order to remove gases.

Step 2 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed.

Step 3 Carbon monoxide gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

If the carbon monoxide gas is 1000 ppm, the concentration of carbon monoxide in the chamber will be 1000 ppm as well.

Step 4 A current was applied to polyaniline pellets in order to measure conductivity before exposure to a gas.

Step 5 After the conductivity of polyaniline pellets reached an equilibrium value, the valve between two chambers (No.3) was opened so that the gas mixture would transfer from the first chamber into the second one due to the difference in the pressure. The feeding step stopped when the pressure of the chamber became 1 atm as well as that of the second chamber.

The concentrations of carbon monoxide gas in chamber No.1 and No.2 are still 500 ppm.

Step 6 The valve between two chambers (No.3) was closed.

Step 7 The voltage drop was detected until the response became saturated. The voltage drop was converted to specific conductivity by using Equation 1.

Step 8 The valve between the second chamber and the vacuum pump (No.4) was opened and then the gas in the second chamber was evacuated by using a vacuum pump.

Step 9 The valve between the second chamber and the vacuum pump (No.4) was closed.

Step 10 Nitrogen gas was fed into the first chamber until the pressure of the first chamber was 2 atm.

The concentrations of both gases will be 500 ppm.

Step 11 Repeated the operating procedure from step 5 to step 9.

The concentrations of both gases in both chambers was 250 ppm.

The difference in the change of electrical conductivity ( $\Delta\sigma$ ) at various doping ratios and be calculated by Equation (4) following;

$$\Delta\sigma = \sigma_{\text{air}} - \sigma_{\text{CO}} \quad (4)$$

where

- $\Delta\sigma$  = the sensitivity (S/cm)
- $\sigma_{\text{air}}$  = the specific conductivity in air (S/cm)
- $\sigma_{\text{CO}}$  = the specific conductivity in CO (S/cm).