

## CHAPTER III

### EXPERIMENTAL PART

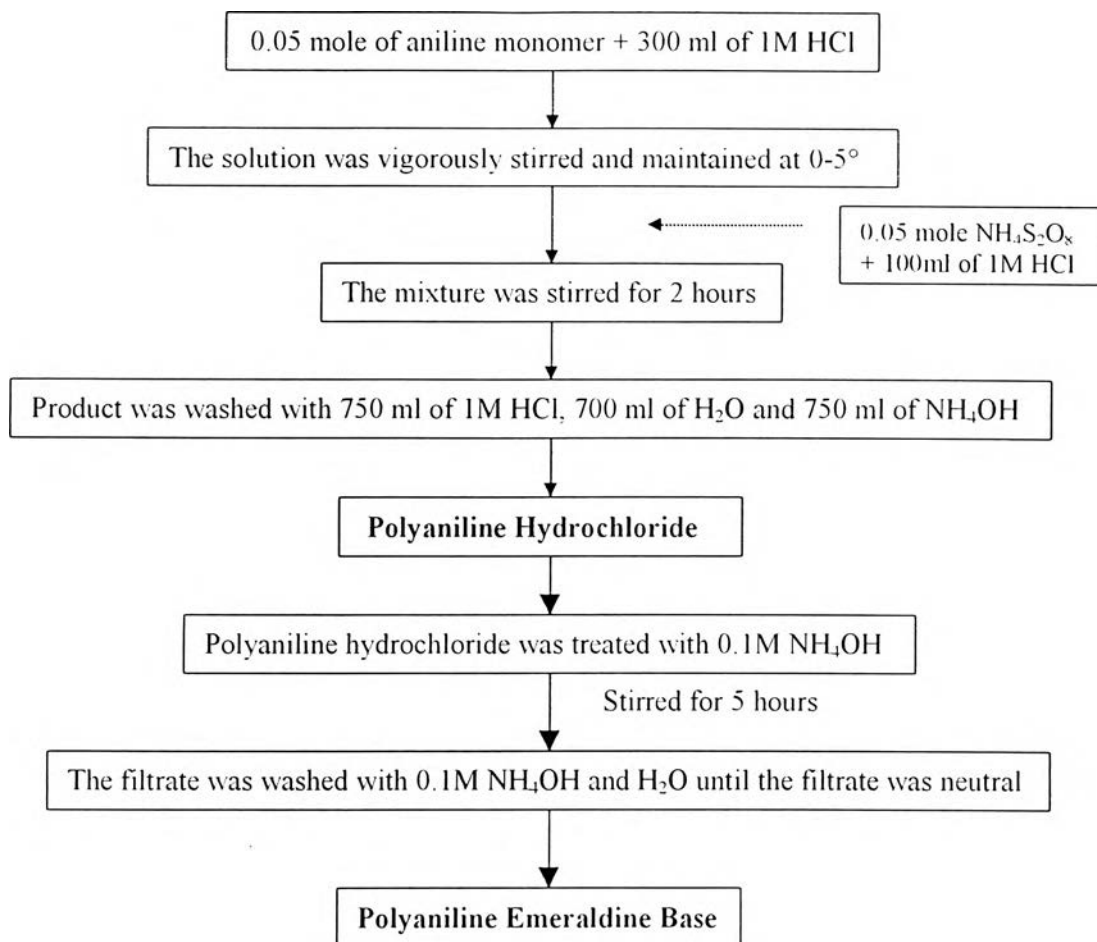
#### 3.1 Materials

Aniline monomer (Merck) was purified by distillation under the reduced pressure, and kept under the N<sub>2</sub> atmosphere at 5°C. Ammonium peroxydisulphate (Merck) was used as an oxidant. HCl (BDH Laboratory), H<sub>3</sub>PO<sub>4</sub> (J.T.Baker), CH<sub>3</sub>COOH (Lab Scan), C<sub>5</sub>H<sub>11</sub>COOH (Fluka) were used as acid dopants as received. N-methyl-2-pyrrolidone (Lab Scan) was used for dissolving polyaniline in order to study UV-Visible spectroscopy and to cast polyaniline films.

#### 3.2 Methodology

##### 3.2.1 Synthesis of Polyaniline Emeraldine Base

In this work, polyaniline emeraldine base was synthesized by the method of *Yen Wei* (1992). Polyaniline emeraldine base was synthesized by an oxidative polymerization of aniline in 1 M aqueous HCl. Ammonium peroxydisulphate was used as an oxidant. The procedure is shown in Figure 3.1



**Figure 3.1** Flow chart of synthesis of polyaniline emeraldine base.

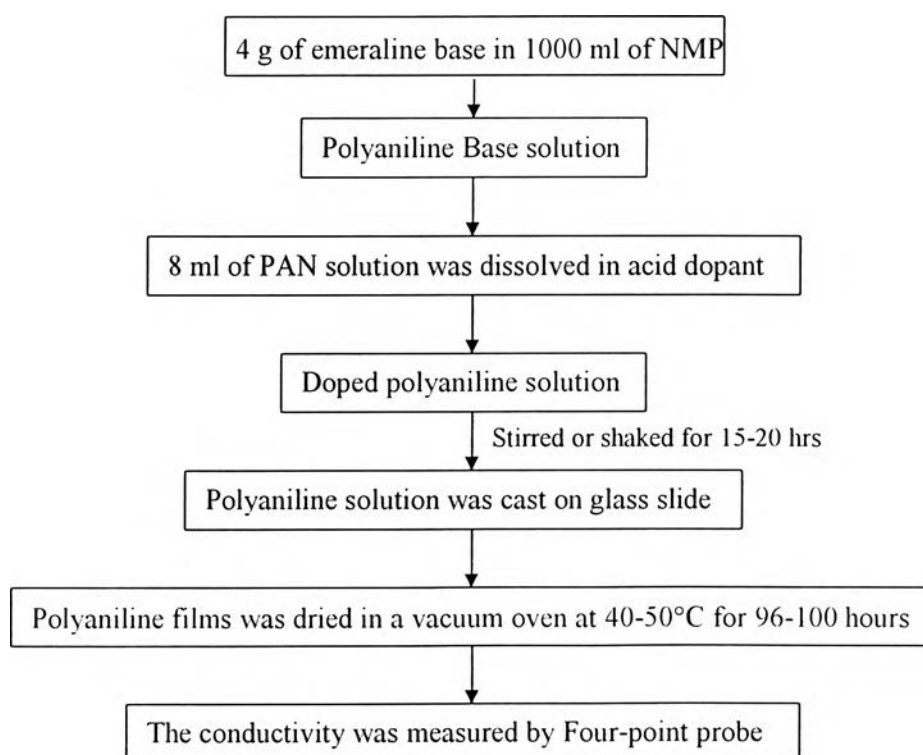
Aniline monomer was purified by distillation under reduced pressure and kept under nitrogen atmosphere. 0.05 mole of aniline monomer was dissolved in 300 ml of 1M HCl and cooled at 0-5 °C in an ice bath. 0.01 mole of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was dissolved in 100 ml of 1 M HCl, then it was slowly added into the previous aniline solution and the mixture was vigorously stirred for 2 hours at 0-5 °C. The polyaniline hydrochloride was filtrated and repeatedly washed with 750 ml of 1 M HCl, 700 ml of  $\text{H}_2\text{O}$  and 750 ml of  $\text{NH}_4\text{OH}$  until the filtrate was colorless. Polyaniline hydrochloride was treated with 500 ml of 0.1 M  $\text{NH}_4\text{OH}$  to convert it to emeraldine base, which was then vigorously stirred for 5 hours. The product (polyaniline emeraldine base) was filtrated and washed with 750 ml of 1 M  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}$  until the filtrated was neutral.

Polyaniline emeraldine base powder was stored in a dessicator at room temperature and was characterized by FT-IR, UV-Visible, SEM, XRD, TGA and a four-point probe for electrical conductivity measurement.

### 3.2.2 Preparation of Doped Polyaniline Emeraldine Salt

The polyaniline base solution was prepared by dissolving 4 g of polyaniline emeraldine base in 1000 ml of N-methyl-2-pyrrolidone and stirring for 5 hours at room temperature.

Doped polyaniline, a conductive form, was prepared by mixing 8 ml of polyaniline solution with acid dopant of a particular concentration. Then the solution was stirred or shaken for 15-20 hours at room temperature. 0.5 ml of doped polyaniline was cast on glass slide and the solvent was evaporated out by drying in a vacuum oven for 96-100 hours at 40-50 °C.



**Figure 3.2** The schematic of doping emeraldine base with acid dopant.

### 3.3 Characterization and Sample Preparation

#### 3.3.1 Ultraviolet-visible spectrometer (UV-VIS)

The ultraviolet-visible spectra of polyaniline were recorded with an UV-Visible spectrometer (Perkin-Elmer, Lambda 10) in order to observe the polaron and bipolaron states of polyaniline emeraldine salt (doped poly aniline). The light source of the uv-visible spectrometer was a deuterium lamp. N-methyl-2-pyrrolidone was used to dissolve polyaniline. The sample solution for uv-visible detection was prepared by pipetting the polyaniline solution for a volume of 10 ml and using N-methyl-2-pyrrolidone at the concentration of 0.1 g/l. The sample solution was viewed microscopically for centering and aperturing to a chamber, then the transmission light was passed to a dispersive system. The light transmission or absorbance was recorded as a function of wavelength in the range of 300-900 nm.

The absorptions of the polaron and bipolaron states are frequently considered in the electron per unit, so the absorption wavelength was converted to photon energy by the Einstein's equation:

$$E = h\nu = \frac{hc}{\lambda} \quad (3.1)$$

where E is photon energy (J), h is Plank's constant which is equal to  $6.62 \cdot 10^{-34}$  J-sec,  $\nu$  is the frequency (Hz or  $\text{sec}^{-1}$ ), c is the light velocity in vacuum, which is equal to  $3 \cdot 10^8$  m/sec and  $\lambda$  is the wavelength (m) of the light.

#### 3.2.2 Fourier Transform Infrared Spectrometer (FT-IR)

FT-IR spectra of polyaniline were recorded from FT-IR spectrometer (Bruker, FRA 106/S) in order to identify important functional groups of undoped polyaniline and doped polyaniline films. The FT-IR spectra in this study were obtained in the absorbance mode with 20 scans at a

resolution of  $4\text{ cm}^{-1}$ , in a range of  $400\text{-}4000\text{ cm}^{-1}$ . A deuterated triglycine sulfate detector (DTGS) was used.

Spectra grade KBr (Carlo Erba) was used as a background. KBr was pelletized by using a hydraulic valve press. Then it was quickly transferred to the FT-IR chamber. After the background spectrum was obtained, the sample was mixed with dried KBr. The mixture was ground and pelletized into a pellet shape by using hydraulic press and transferred to the sample holder using the same procedures as mentioned above.

### 3.3.3 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (JOEL 5200) was used to observe the morphology of polyaniline films. SEM digitized photographs were obtained with magnifications between 35-20,000 times.

Samples of doped polyaniline films were prepared as mentioned in the section 3.2.2. The sample films were cut into 0.3 cm to 0.3 cm and put to a brass-stub by using an adhesive tape. Polyaniline films were coated with a thin Au film by a vacuum evaporation and placed into the specimen stage inside the microscope chamber. The morphology of polyaniline films was obtained by using an acceleration voltage of 25 kV with a magnification of 5000 times.

### 3.3.4 Thermal Gravimetric Analyzer (TGA)

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to study the thermal stability and decomposition temperature of undoped and doped polyaniline films.

Polyaniline films were prepared by the method of Section 3.2.2. The films were removed from glass slides and weighed in the range of 5-10 mg. The samples were loaded into a platinum pan and held on the platinum

wire, the furnace chamber was closed and the polyaniline films were heated from 25°C to 750°C with a heating rate of 20°C/min.

### 3.3.5 X-Ray Diffractometry (XRD)

An X-Ray diffractometer (Rigaku model) was used to study the diffraction pattern and degree of crystallinity of undoped polyaniline (emeraldine base) and doped polyaniline (emeraldine salt) films. The polyaniline films were placed into the holder and the measurements were run in the continuous mode with a scan speed of 5 degree/minute from 5 to 50 degrees. Cu K-Alpha1 was used as a X-ray source and K-Beta was used as a filter.

## 3.4 Electrical Properties

### 3.4.1 Probe for Characterization of Sheet Resistance ( $R_s$ )

The Four-Point probe technique is generally used to measure the specific conductivity of thin films. The schematic of four-point probe used in this experiment is shown in Figure 3.3. Probe tips made from stainless steel were pressed against the surface of the polyaniline film. The specific conductivity was obtained by applying the current (I) through probe 1 and 2, and measuring the voltage (V) between probe 3 and 4. The specific conductivity was calculated from equation 3.2:

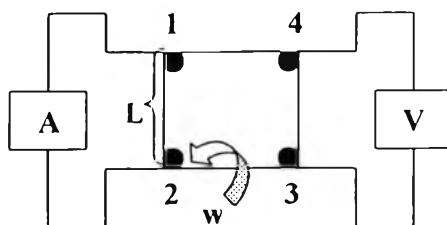


Figure 3.3 Schematic of Four-Point probe used in this experiment.

$$\sigma = \frac{1}{\rho} = \frac{I}{K \times V \times t} \quad (3.2)$$

where  $\sigma$  is the specific conductivity (S/cm),  $\rho$  is the specific resistivity ( $\Omega$  cm),  $I$  is the current which was applied through probe 1 and 2,  $K$  is the geometric correction factor which is equal to the diameter of probe tip ( $w$ ) divided by probe tip spacing ( $l$ ),  $\frac{w}{l}$ . The geometric correction factor was obtained from standard materials with known specific resistivities (Appendix B). Silicon wafers were used as standard material.  $V$  is the voltage between probe 3 and 4 and  $t$  is the thickness of polyaniline films (cm).