

CHAPTER III

EXPERIMENTAL PART

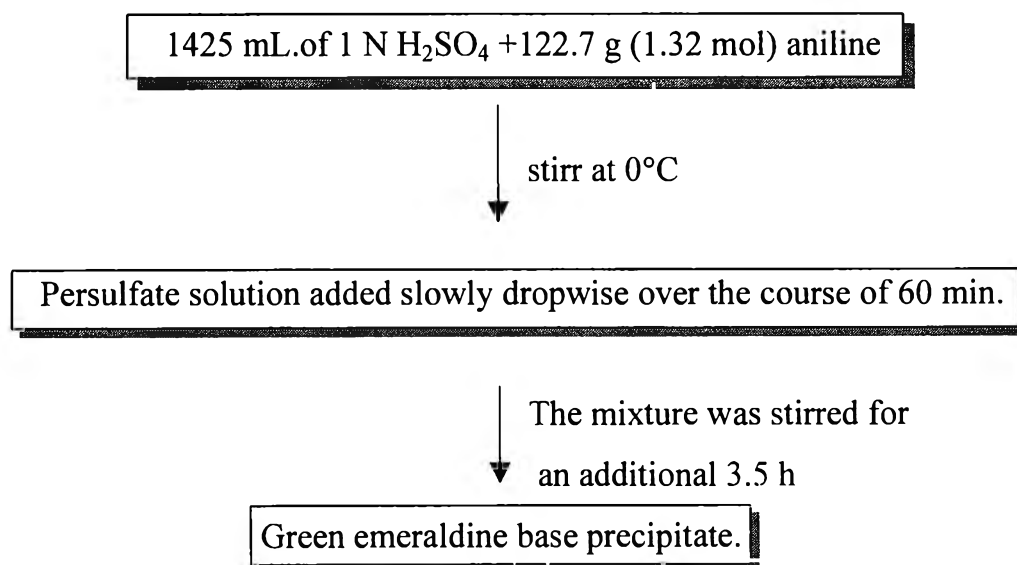
3.1 Materials.

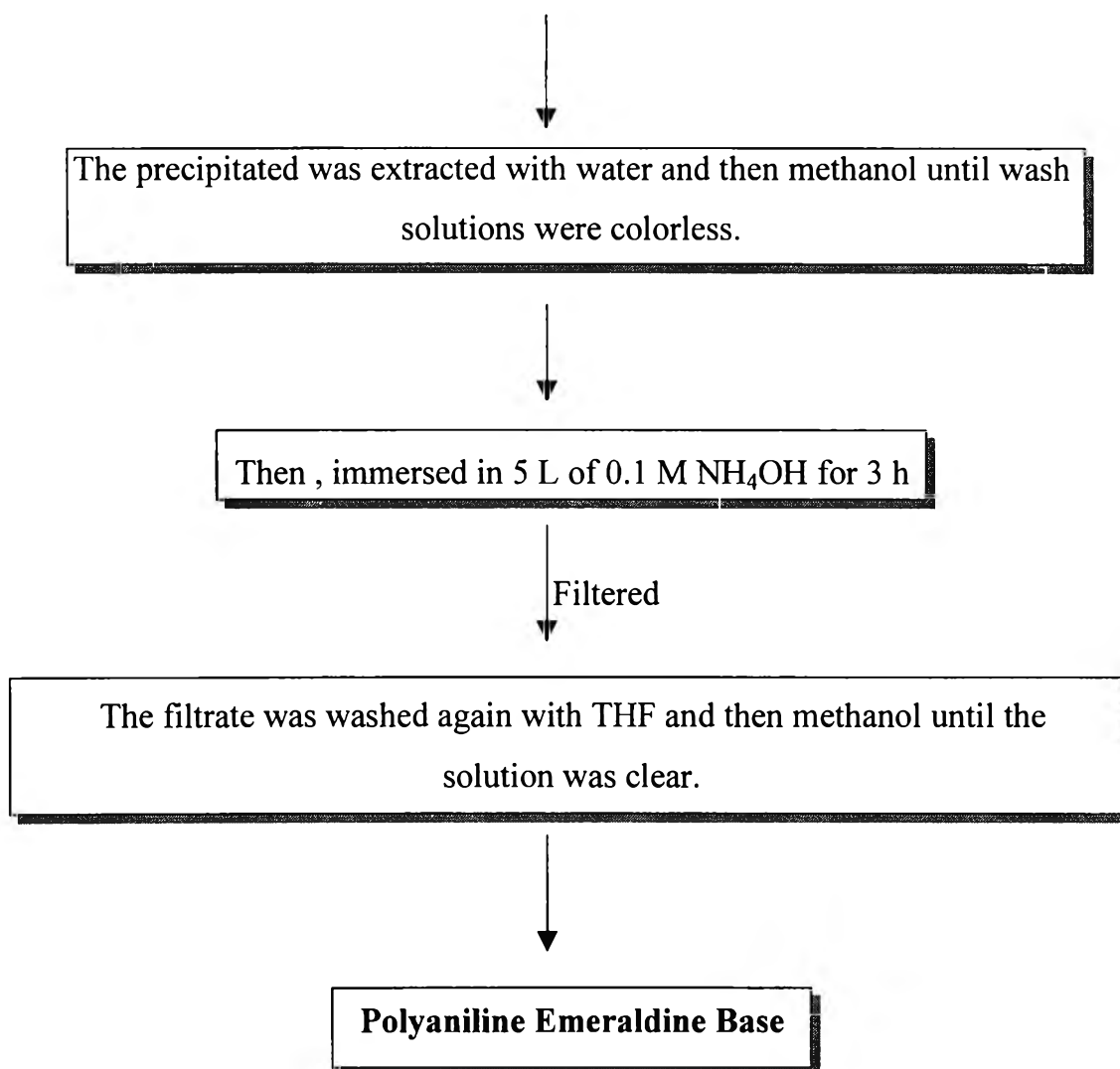
Aniline monomer (Merck) was purified by distillation under the reduced pressure, and kept under the N_2 atmosphere at $5^\circ C$. Ammonium peroxidisulphate (Merck) was used as an oxidant. H_2SO_4 (Lab Scan), $HCOOH$ (BDH), HNO_3 (Lab Scan), CSA (Fluka) were used as acid dopants as received. N-methyl-2-pyrrolidone (Lab Scan) was used for dissolving polyaniline in order to study UV-Visible spectroscopy.

3.2 Methodology.

3.2.1 Synthesis of Polyaniline Emeraldine Base.

In this work, polyaniline emeraldine base was synthesized by the method of *Winokur., M.J.* (1998). Polyaniline emeraldine base was synthesized by an oxidative polymerization of aniline in 1 M aqueous H_2SO_4 , replacing HCl in order to study the molecular weight effect. Ammonium peroxidisulphate was used as oxidant. The procedure was shown in Scheme 3.1.





Scheme 3.1 Flow chart of synthesis of polyaniline.

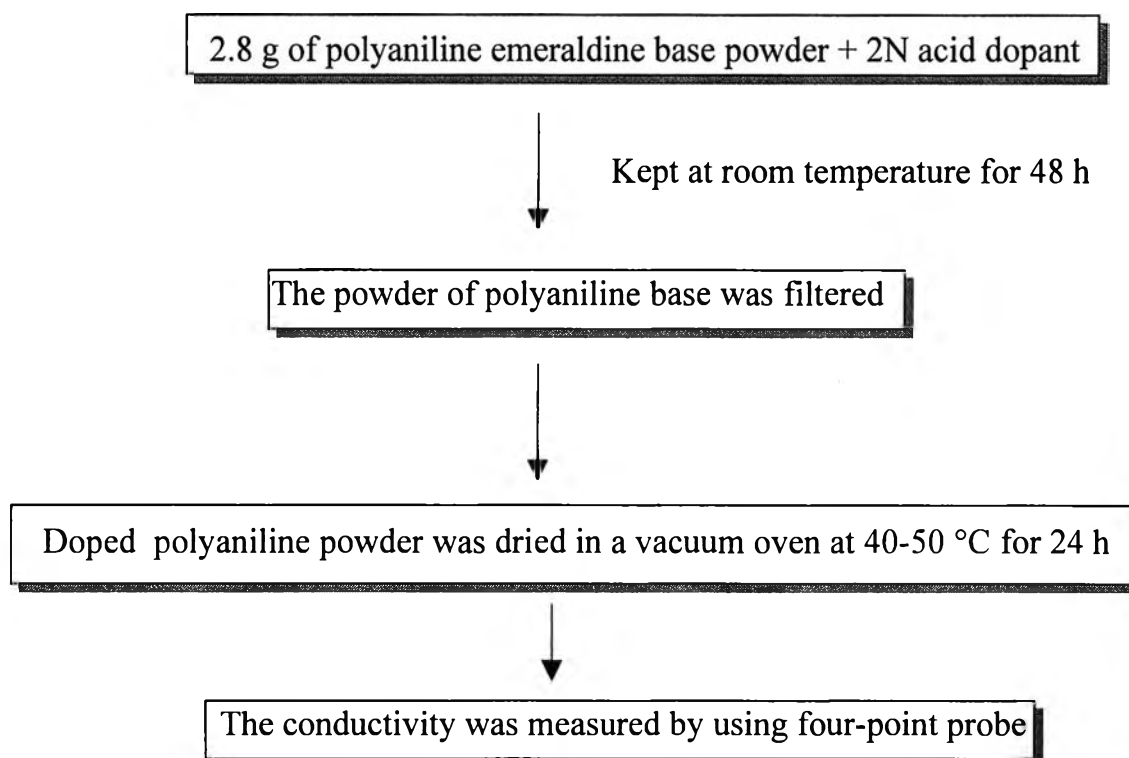
Aniline monomer was purified by a distillation under reduced pressure and kept under nitrogen atmosphere. 122.7 g (1.32 mol) of aniline monomer was dissolved in 1425 ml. of 1 N H_2SO_4 and cooled at $0-5^\circ\text{C}$ in an ice bath with stirring. In a separate flask, 1575 mL of 1 N H_2SO_4 was combined with 69.03 g of ammonium peroxodisulfate. The sulfate solution was cooled to 0°C and then slowly added dropwise to the aniline solution by means of an addition funnel over the course of an hour. The combined solutions was allowed to react for an additional 3.5 hr. The green emeraldine base precipitate was collected in a large Buchner funnel. The powder was extracted first in

water and then in methanol until the wash solutions were colorless and finally filtered. This as-synthesized polyemeraldine salt was subsequently immersed in 5 L of 0.1 M NH_4OH for 3 h, filtered, and then washed once again with THF and methanol until the solutions were clear. The purified emeraldine was vacuum dried ($<10^{-5}$ torr) and stored in a desiccator at room temperature and was characterized by FT-IR, UV-Visible, SEM, XRD, TGA, particle size analyzer and a four-point probe for electrical conductivity measurement.

3.2.2 Doping Procedure of Polyaniline Emeraldine Base.

The doped polyaniline emeraldine base powder was prepared by mixing of 2.8 g of polyaniline emeraldine base powder with various amounts of 2 M acid dopant. Then, the mixture was kept at room temperature for 48 hours. The doped polyaniline powder was obtained by filtering and was dried at 80°C under a vacuum oven for 24 hours.

The schematic of doping of polyaniline emeraldine base was shown in Scheme 3.2.



Scheme 3.2 Doping of polyaniline emeraldine base

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 16) in order to observe the polaron and bipolaron states of polyaniline emeraldine salt (doped polyaniline). 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 measurement was prepared by weighing polyaniline powder 0.01 g in 100 ml volumetric flask and using N-methyl-2-pyrrolidone as solvent and leave it stir at room temperature until it completely dissolved. The sample solution was viewed microscopically for entering 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 250-900 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 6.62×10^{-34} J-sec, ν is the frequency (Hz or sec^{-1}), c is the light velocity in vacuum, which is equal to 3×10^8 m/sec and λ is the wavelength (m) of the light.

3.3.2 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 powder. The FT-IR spectra in this study were obtained in the absorbance mode with 64 scans at a resolution of

$\pm 4\text{cm}^{-1}$, 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. The sample was pressed under 8 kg/cm^2 for 2 minutes. Then it was transferred to the FT-IR chamber. After the background spectrum was obtained, the sample was mixed with the dried KBr. The mixture was ground and pelletized into pellet shape by using hydraulic press and transferred to the sample holder in the chamber. The diameter of sample is 1 cm. and thickness is about 0.005 cm.

3.3.3 Scanning Electron Microscope (SEM).

Scanning Electron Microscope (JOEL 5200) was used to study the morphology of polyaniline powder and pellets. SEM digitized photographs were obtained with magnifications between 35-20000 times

Samples of doped polyaniline powder were prepared as mentioned above in the section 3.2.2. The polyaniline pellets were prepared by using a hydraulic press. The polyaniline powder and pellet were put on the brass-stub by using an adhesive tape. The prepared samples were coated with a thin layer of Au by using a vacuum evaporation and placed into the specimen stage inside the microscope chamber. The morphology of polyaniline powder and pellet was obtained by using an accelerator voltage of 25 kV with a magnification of 3500 times.

3.3.4 Thermal Gravimetric Analyzer (TGA).

A thermal gravimetric analyzer (Dupont, Model TGA 2950) was used to study the thermal stability and the decomposition temperature of undoped and doped polyaniline pellets.

Polyaniline powder was prepared by method of section 3.2.2. The powder of polyaniline was weighed in the range of 2-3 mg. The sample was loaded into a platinum pan and held on a platinum wire, the furnace chamber

was closed and the polyaniline powder was heated from 30°C to 750°C with a heating rate of 10°C/min.

3.3.5 X-Ray Diffractometry (XRD).

An X-Ray diffractometer (Rigaku Model) was used to study the diffraction pattern and the degree of crystallinity of undoped and doped polyaniline powders. The powder was placed into a sample holder and the measurement was continuously run with a speed of 5 degree/minute from 5 to 50 degrees. Cu K-alpha was used as a X-ray source and K-beta was used as a filter.

3.3.6 Particle Size Analyzer.

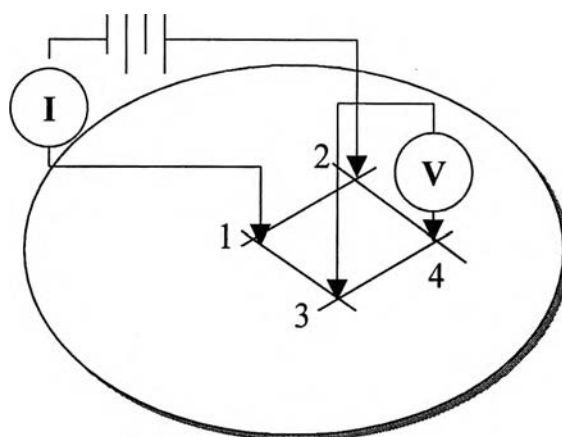
Particle Size Analyzer (Mastersizer X) was used to investigate the particle size of polyaniline. The powder of polyaniline both before and after milling were dropped in the water bath containing dispersing agent. The particle size was observed by using lens with a magnification of 300 times. Ultrasonic action was available to disperse cohesive materials and surfactants might be easily applied to prevent flocculation. Both stirring and pumping speeds were controlled to allow the optimum transport and de-aggregation to be obtained.

3.4 Electrical Properties.

3.4.1 Probe for Characterization of Sheet Resistance (R_s).

The four-point probe technique was generally used to measure the sheet resistivity that measures of the ability of a layer to resist the conduction of electrical carriers within a thin film which can be converted into the specific conductivity. The schematic of four-point probe used in this work is shown in the Scheme 3.3. Probe tips made from silver were pressed against the surface of the polyaniline pellets. The specific conductivity was obtained by introducing a current I through pin numbers 1 and 2 and determining the

voltage drop V across the pin numbers 3 and 4. The specific conductivity was calculated from equation 3.2 :



Scheme 3.3 Schematic of four-point probe.

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

where σ is the specific conductivity (S/cm), ρ is the specific resistivity (Ω .cm.), I is the current (mA) 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), w / l . The geometric correction factor was obtained from standard materials, silicon wafers, whose specific resistivities are known. V is the voltage drop (mV) between probes 3 and 4 and t is the thickness of polyaniline pellets (cm). The calibration procedure details are given in Appendix A and B.