

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

Analytical grade aniline, purchased from Merck Co., Ltd, was used as the monomer. Ammonium Peroxodisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, of analytical grade, purchased from Merck Co., Ltd, was used as an oxidant. Twenty five percent of ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$), of analytical grade, purchased from Merck Co., Ltd, was used as the base reagent. Calcium hydride (CaH_2), of analytical grade, purchased from Fluka Co., Ltd, was used in drying aniline monomer. Thirty seven percent of hydrochloric acid (HCl), of analytical grade, purchased from Merck Co., Ltd, was used as the protonic acid in doping process. 1-methyl-2-pyrrolidone ($\text{H}_3\text{N}(\text{CH}_2)_3\text{C}=\text{O}$, NMP) of analytical grade, purchased from Merck Co., Ltd, was used as a solvent for preparation polyaniline thin film. Nitrogen gas (N_2), of UHP grade with 99.9 % purity, was purchased from Thai Industrial Gases Public Company Limited (TIG). The 500-ppm of sulfur dioxide (SO_2) balance with nitrogen was purchased from Thai Industrial Gases Public Company Limited (TIG).

2.2 Methodology

2.2.1 Purification of Aniline Monomer

Aniline monomer was purified according to the method of Perrin (1985).

Procedures: 100 ml of aniline monomer was dried with 0.25 grams of calcium hydride (CaH_2) for 30 minute. The dried aniline was twice distilled in reduced pressure at 60°C . The colorless of aniline was obtained and stored in nitrogen atmosphere at 0°C prior to use. A scheme of the apparatus for distillation method is shown in Figure 2.1.

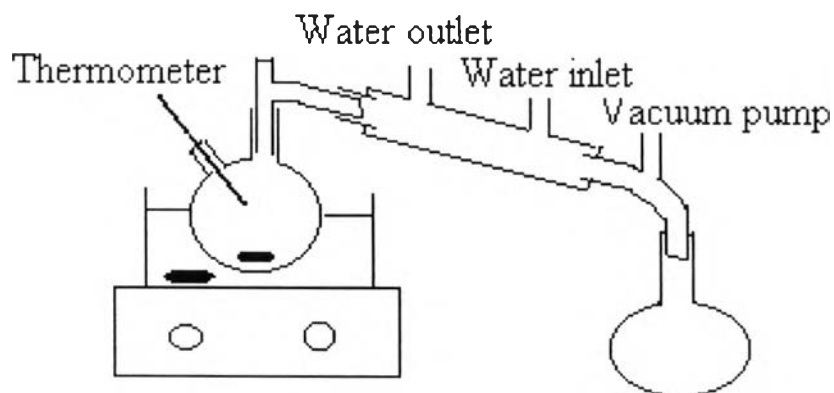


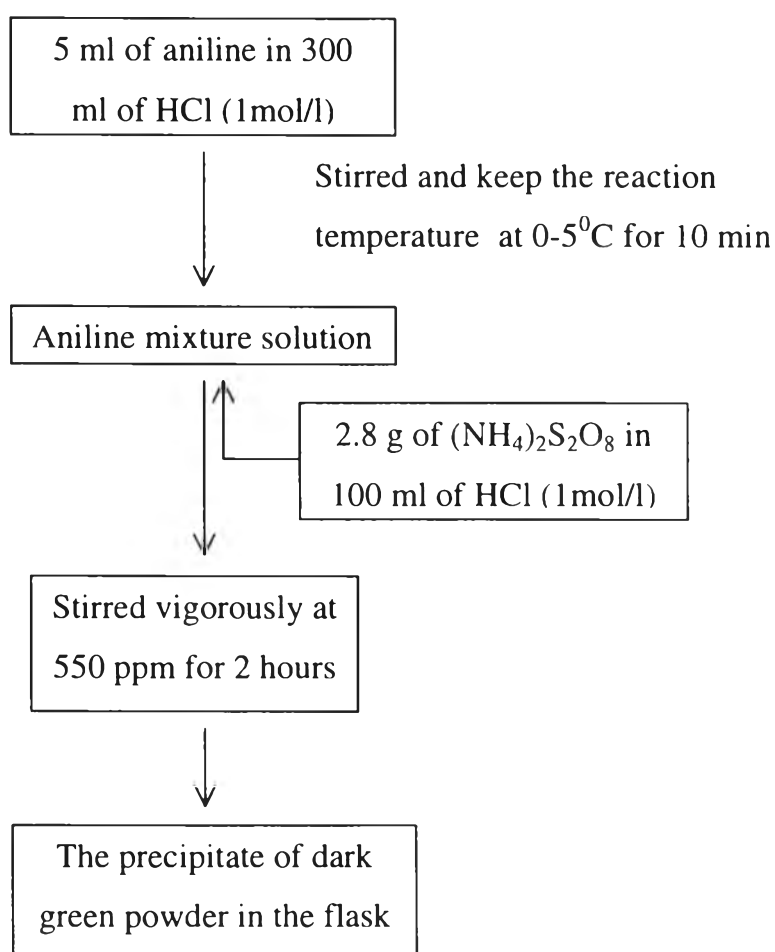
Figure 2.1 A scheme of the apparatus for distillation method.

2.2.2 Synthesis of Polyaniline Emeraldine Base

Polyaniline in the form of emeraldine base was synthesized chemically according to the method of MacDiarmid (1991).

Procedure: 300 ml of HCl (1mol/l) containing 5 ml of aniline was cooled at $0-5^\circ\text{C}$. A mixture solution of 2.8 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 100 ml of HCl (1mol/l) was added very slowly into the mixture of aniline solution within 30 minutes. The mixture solution was stirred vigorously at 550 rpm for 2 hours. The dark green precipitate of polyaniline emeraldine salt was recovered from the polymerization flask, filtered and then washed with 600 ml of HCl (1mol/l), 600

ml of water and followed by 750 ml of NH_4OH (0.1mol/l). Polyaniline emeraldine salt was converted to the emeraldine base form by stirring the emeraldine salt form in 500 ml of NH_4OH (0.1mol/l) for 5 hours. The dark blue powder of polyaniline emeraldine base was filtered and washed by using 750 ml of NH_4OH (0.1mol/l) and water until the filtrate was neutral. The dark blue powder of polyaniline emeraldine base was dried in a vacuum oven at 60°C for 12 hours. A diagram of synthesis method is shown in Figure 2.2.



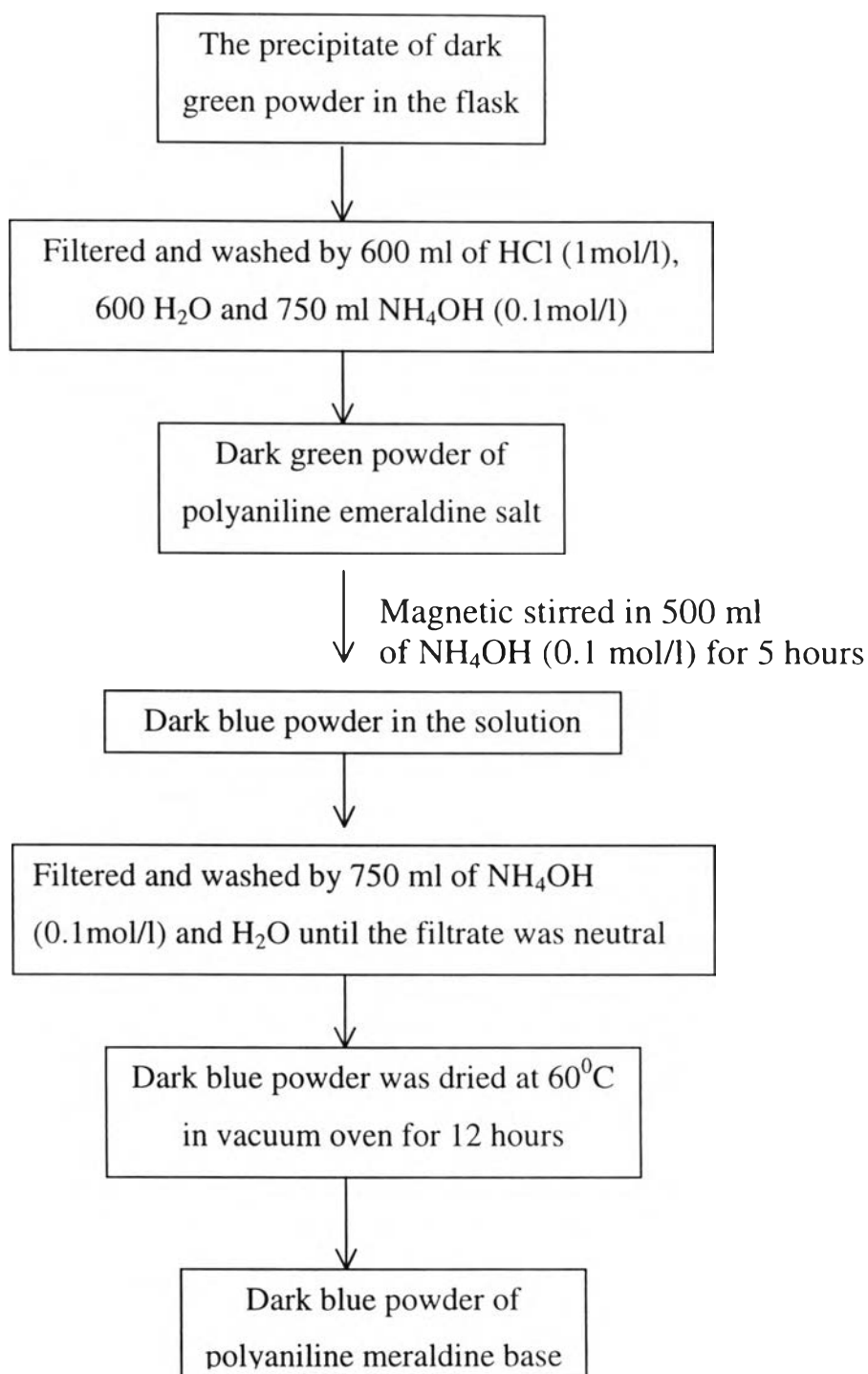


Figure 2.2 A diagram of Synthesis of Polyaniline.

2.3 Characterization Techniques/ Sample Preparations

2.3.1 Fourier-Transform Infrared Spectrometer (FTIR)

FTIR was used to identify the functional group characteristic of the synthesized polyaniline and the differences in the functional group between the undoped and doped polyaniline films.

Infrared spectrum was recorded on a Bruker FRA 106/S in the wavenumber range of 400-4000 cm^{-1} using the transmittance mode. The resolution of this instrument was $\pm 4 \text{ cm}^{-1}$. The sample chamber was purged with nitrogen for 20 minute to remove carbon dioxide gas before recording the sample spectrum. The KBr technique was used to prepare the powder samples and films for recording spectrum.

Procedure for preparation synthesized polyaniline powder:

Specimens for the synthesized polyaniline were prepared by grinding powdered polyaniline with KBr powder in the ratio of 1:20. The sample mixture was pressed with special dies under a pressure of 10 tons. The sample spectrum was recorded by using KBr as a background.

Procedure for preparation polyaniline film samples:

Polyaniline films were prepared by dissolved the synthesized polyaniline in NMP at the concentration of 4 g/l. The mixture solution of polyaniline was divided into 8 ml/sample for 10 samples. A 0.15 ml of HCl at particular concentrations of 0, 1.3×10^{-2} , 2.6×10^{-2} , 7.0×10^{-2} , 1.3×10^{-1} , 1.8×10^{-1} , 2.6×10^{-1} , 5.3×10^{-1} , 8.8×10^{-1} or 1.3 mol/l was added into the polyaniline solution. The ratio of C_a/C_p is the ratio of HCl concentration in g/l divided by polymer concentration in g/l in the mixture solution. The ratios of C_a/C_p of polyaniline solution were 0, 0.73, 1.46, 4.0, 7.3, 10.2, 14.6, 30, 50 and 73. The mixture solutions were allowed to reach equilibrium during a period of 15-20 hours. A 0.4 ml of each mixture solution

was cast on a glass substrate with sizes of $2.5 \times 2.5 \text{ cm}^2$. The wet films were dried at $40\text{-}50^\circ\text{C}$ for 96-120 hours in a vacuum oven. The undoped and doped polyaniline films were obtained and used in FTIR characterization. Specimens for polyaniline films were prepared by grinding 0.0065 grams of films sample with 0.21 grams of KBr. The mixture samples were pressed with special dies under a pressure of 10 ton. The film spectra was recorded by using KBr as a background.

2.3.2 UV-visible Spectrophotometer (UV-Vis)

UV-visible spectrophotometer was used to investigate the important characteristic of the synthesized polyaniline and the differences in the electronic structure between the undoped and doped polyaniline films. The absorption spectra of the excitation of benzenoid segments, quinoid segments, and polaron state were identified. UV-visible spectra were performed on a Perkin Elmer Lambda 10 spectrometer in the wavelength range of 300-1000 nm.

Procedure for preparation synthesized polyaniline powder:

The synthesized polyaniline powder was dissolved in NMP at the concentration of $3.1 \times 10^{-3} \text{ g/l}$. A 4 ml of the mixture solution was put in the quart cell and recorded the UV-visible spectra by using NMP as a background.

Procedure for preparation polyaniline film samples: The undoped and doped polyaniline film samples were prepared by dissolved the synthesized polyaniline in NMP at the concentration of 0.8 g/l. A 0.15 ml of HCl at particular concentrations of 0, 2.6×10^{-3} , 5.1×10^{-3} , 1.4×10^{-2} , 2.6×10^{-2} , 3.6×10^{-2} , 5.1×10^{-2} , 1.1×10^{-1} or $1.8 \times 10^{-1} \text{ mol/l}$ was added to 8 ml of the polyaniline solution. These mixture solutions had the C_a/C_p ratios of 0, 0.73, 1.46, 4.0, 7.3, 10.2, 14.6, 30 and 50 respectively. These mixture solutions were allowed to reach equilibrium during a period of 15-20 hours. A 0.25 ml of the solution was cast on

a glass substrate. The wet films were dried as the same condition as in FTIR film preparation. Polyaniline films spectra were recorded by using the glass slide spectra as a background.

The absorption of the polaron state of the doped polyaniline is usually monitored in the unit of electron volt. Therefore the absorption wavelength is changed to the electron volt unit by using the Einstein's equation. The phonon energy in Joule (J) can be converted to electron volt unit by dividing with 1.602×10^{-19} J/eV. Einstein's equation is shown in equation (2.1):

$$E = h \nu = \frac{hc}{\lambda} \quad (2.1)$$

where

- E = photon energy (J)
- h = Planck's constant = 6.62×10^{-34} J.sec
- ν = Frequency (Hz or sec^{-1})
- c = light velocity in vacuum = 3×10^8 m/sec
- λ = Wavelength (m)

2.3.3 Elemental Analysis (EA)

Elemental analysis was used to determine the elements of carbon (C), hydrogen (H) and nitrogen (N) atoms in the synthesized polyaniline and the doping level of the doped polyaniline films at the various acid concentrations. The experiment was performed on Perkin-Elmer 2400 Series II CHNS/O Analyzer.

Procedure: The doped film samples were prepared as the same concentration as in FTIR films. The film samples was weighed at 1.5–2.5 mg and sealed in the tin capsules and put in the sample cell. The sample was dropped in

the combustion zone at temperatures between 975-1100⁰ C with helium as a carrier gas. In the combustion zone, oxide of carbon (C), hydrogen (H) and nitrogen (N) and the others elements, sulfur (S) and chlorine (Cl), was scrubbed with Lead-chromate and glass wood. In the reduction zone, oxide of carbon (C), hydrogen (H) and nitrogen (N) was reduced with copper (Cu) to carbon (C), hydrogen (H) and nitrogen (N) atoms at temperatures between 550-640⁰ C. Therefore the amounts of carbon (C), hydrogen (H) and nitrogen (N) were determined.

The doping level of the doped films was calculated from the weight ratio of Cl/N by using Equation 2.2:

$$\% \text{ Doping Level} = \frac{\text{Cl}}{\text{N}} \times \frac{M_{\text{N}}}{M_{\text{Cl}}} \times 100 \quad (2.2)$$

where

- Cl = mass of Cl calculated from the EA data
- N = mass of N from Elemental Analyzer (EA)
- H = mass of H from Elemental Analyzer (EA)
- M_N = molecular weight of N = 14.01 g/mol
- M_{Cl} = molecular weight of Cl = 34.45 g/mol

2.3.4 Scanning Electron Microscope (SEM)

Scanning electron microscope was used to identify the microstructure of the undoped and doped polyaniline thin films. The film thickness was also measured by using SEM. The samples were characterized by JOEL Scanning Electron Microscope model JSM-5200.

Procedure: The doped polyaniline films were prepared as the same condition as in FTIR films. The film sample was cut in to small piece and adhered on a brass-stub by using adhesive tape. The sample on the stub was coated with thin layer of gold by using JFC-1100 E ion sputtering device.

2.3.5 Thermogravimetric Analyzer (TGA)

Thermal stability of the undoped and doped polyaniline thin film was studied by using TGA. TGA thermogram was recorded on a Perkin-Elementer TGA 7. The small piece of sample with an approximate weight of 1-5 mg was put in to the platinum pan and heated from 30 to 900°C at the heating rate 10°C/min. The sample chamber was exposed to nitrogen and oxygen at the flow rate of 10 ml/min. The mass increase with temperature was recorded.

Procedure: The doped polyaniline film was prepared as the same condition as in FTIR films.

2.2.6 Four Point Probe Technique (Conductive Meter)

The sheet resistivity of thin films was measured by using the Four point probe technique. Four point probe meter consists of two outer electrodes connected with a current driver and two inner electrodes connected with a voltmeter as shown in Figure 2.3.

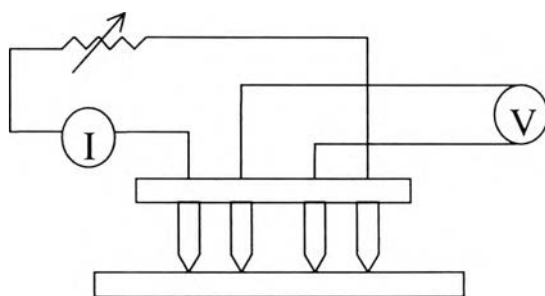


Figure 2.3 A schematic of Four Point Probe Meter.

During the sheet resistant measurement, a constant current was applied to the two outer electrodes and the sample voltage was measured between the two inner electrodes. The sheet resistivity was calculated by using Equation 2.3:

$$R_s = K \times \frac{V}{I} \quad (2.3)$$

where

- R_s = sheet resistivity (Ω)
- K = Geometric correction factor
- V = voltage drop (V)
- I = applied current (A)

The geometric correction factor depends on the type of material for making probes and the distance between the pin. The geometric correction factor can be determined by using the standard sheet that known the specific resistivities. In this work, this geometric correction factor was determined by using silicon wafer chip (SiO) and it was calculated by using Equation 2.4. The specific resistivities of this silicon chip are shown in Appendix a.

$$K = \frac{\rho_{ref}}{R_s \times t} = \frac{I \times \rho_{ref}}{V \times t} \quad (2.4)$$

- ρ_{ref} = known resistivity from the chemical handbook ($\Omega.cm$)
- t = standard sheet thickness

The specific conductivity of doped polyaniline films was calculated from Equation 2.5.

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (2.5)$$

where

- σ = specific conductivity (S/cm)
- ρ = specific resistivity (Ω .cm)
- I = current (A)
- K = Geometric correction factor
- V = Voltage (V)
- t = film thickness (cm)