



CHAPTER III EXPERIMENTAL

3.1 Materials

Analytical grade aniline monomer (Merck) was used as a monomer. Analytical grade ammonium peroxydisulfate (Merck) was used as an oxidant. 25% of analytical grade ammonia solution (Merck) was used as a basic reagent. Analytical grade methanol (Labscan) was used to wash emeraldine base in polyaniline synthesis process. 38% of analytical grade hydrochloric acid (Merck) was used as acid medium in polyaniline synthesis process. Purum 99% camphor-10-sulfonic acid (Fluka), 70% nitric acid (Merck) was used as protonic acid in doping process.

Analytical grades 4,4-oxydianiline (Fluka) and pyromellitic dianhydride (Fluka) were used as precursor for the polyimide synthesis. Analytical grade N-methyl pyrrolidone (Merck) was used as a medium for polyimide synthesis and as a solvent for UV-Visible spectroscopy measurement.

99% of UHP grade N₂ gas (TIG) was used as a carrier gas. 1000 ppm carbon monoxide (CO) balanced with nitrogen (TIG) was used as a target gas.

3.2 Methodology

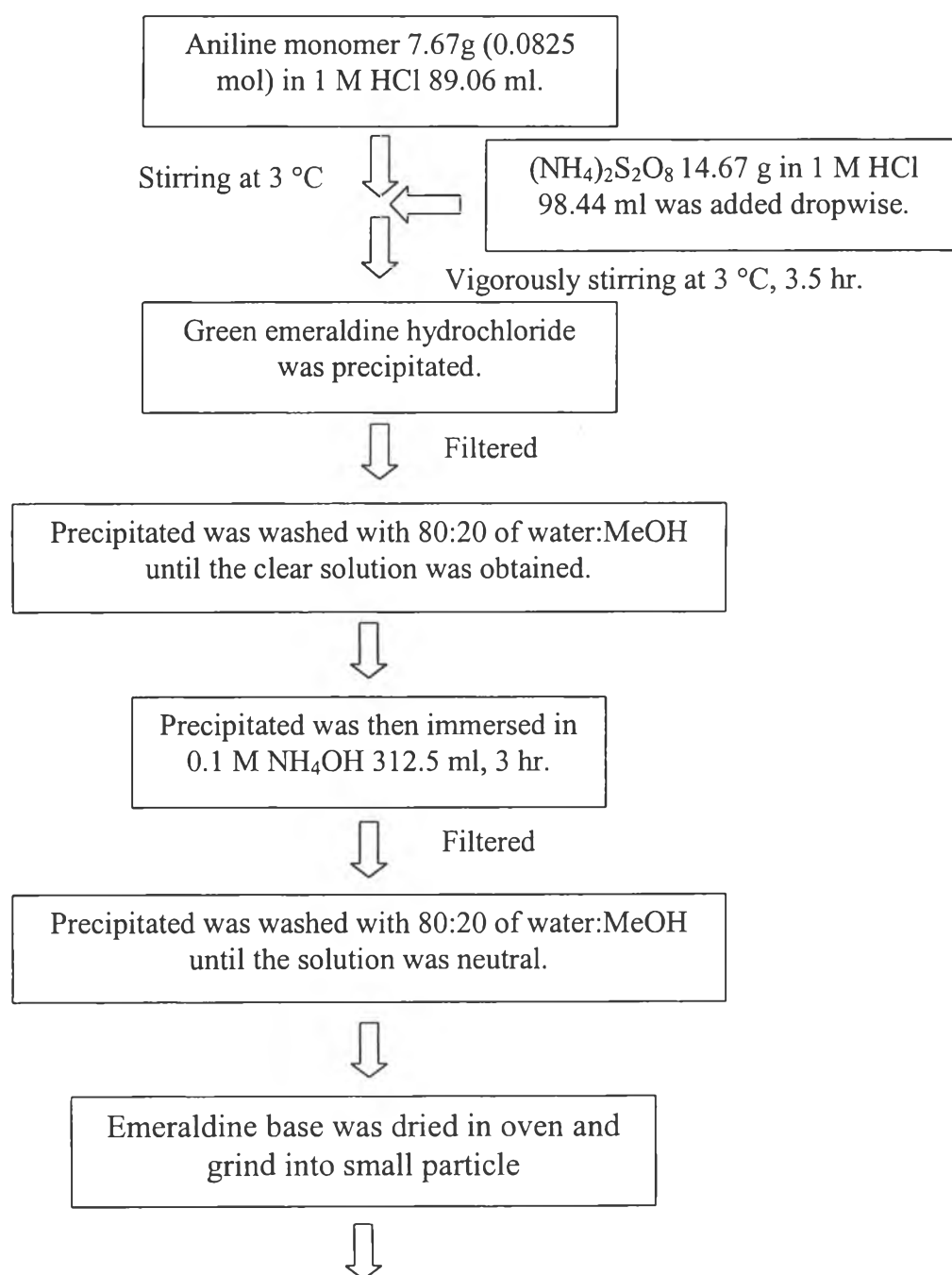
3.2.1 Polyaniline synthesis and doping process

3.2.1.1 *Synthesis of polyaniline*

Aniline monomer was distilled by reduced-pressure distillation method at 58 °C, then it was stored at 0-5 °C and covered with aluminium foil in order to keep it from light.

Polyaniline was synthesized by adding 7.67 g. aniline to 1 M HCl 89.06 ml in 3-neck round bottom reaction flask then (NH₄)₂S₂O₈ 14.67 g in 1 M HCl 98.44 ml was added dropwise into aniline solution within an hour, then the solution was vigorously stirred at 3 °C for 3 hours. Then the green emeraldine hydrochloride

precipitate was obtained. Thereafter, the precipitated was filtered and washed by 80:20 of water:MeOH until the clear solution was obtained. The precipitated was subsequently immersed in 0.1 M NH_4OH 312.5 ml for 3 hours. Then the precipitated was washed with 80:20 of water:MeOH until the solution was neutral. The solid polyaniline was finally collected and dried in vacuum at 50 °C for 12 hours and stored in a vacuum dessicator. The dried emeraldine base was then grinded to very small particles.



Emeraldine salt is dried in vacuum at 50 °C, 12 hr.

Scheme 3.1 Synthesis path of polyaniline.

3.2.1.2 Doping of polyaniline

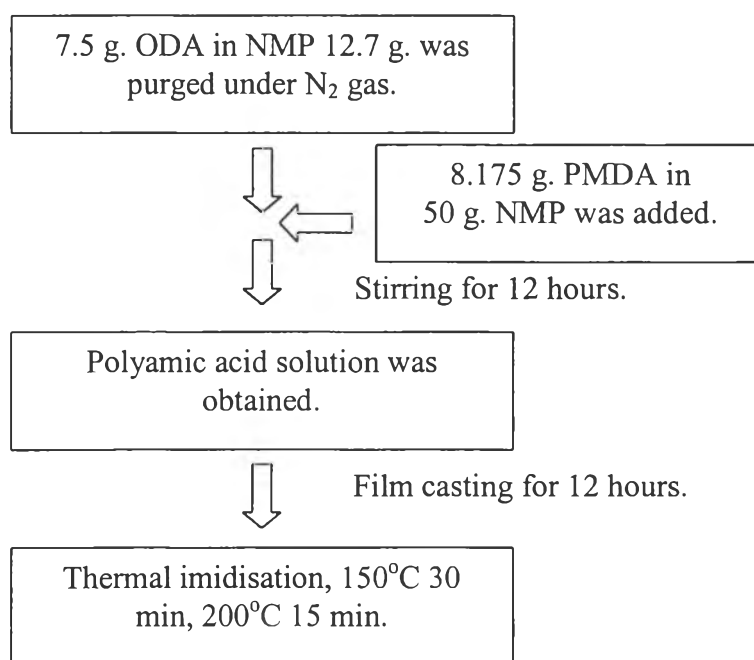
Nitric acid doped polyaniline was prepared by using 1M nitric acid as a stock solution. 1M nitric acid stock solution was prepared by adding 15.84 ml of 70% nitric acid with 234.16 ml of distilled deionized water in 250 ml volumetric flask. 0.1 M nitric acid solution was prepared by adding 10 ml of 1 M nitric acid stock solution with 90 ml of distilled deionized water in 100 ml volumetric flask. Emeraldine base was doped at various ratios of 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 by adding 0.1 M nitric acid solution 2.20, 5.52, 11.05, 22.09, 55.24, 110.48 and 220.96 ml, respectively to 0.4 g of emeraldine base powder.

Camphorsulfonic acid doped polyaniline was prepared by using 1 M camphorsulfonic acid as a stock solution. 1M camphorsulfonic acid stock solution was prepared by adding 23.23 g of camphorsulfonic acid with distilled deionized water in 100 ml volumetric flask. 0.1 M camphorsulfonic acid solution was prepared by adding 10 ml of 1 M camphorsulfonic acid stock solution with 90 ml of distilled deionized water in 100 ml volumetric flask. Emeraldine base was doped at various ratios of 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 by adding 0.1 M camphorsulfonic acid solution 2.20, 5.52, 11.05, 22.09, 55.24, 110.48 and 220.96 ml, respectively to 0.4 g of emeraldine base powder

3.2.2 Polyimide Synthesis

First, 7.5 g of 4,4'-oxydianiline (ODA) was dissolved in 12.7 g. N-methyl-2-pyrrolidone (NMP) under N₂ purging at room temperature with stirring by a mechanical stirrer in a 3-neck round bottom flask. In separate flask, 8.175 g. pyromellitic dianhydride (PMDA) was dissolved in 50 g. NMP with minor heating. Thereafter, PMDA solution was added to the 3-neck round bottom flask in which ODA was dissolved. The solution was stirred continuously with N₂ purging for 12 hours. Finally, poly(amic acid) which is the precursor of polyimide was prepared.

Poly(amic acid) solution was casted on teflon sheet to get poly(amic acid) film. Then the film was imidised in an oven with N₂ gas flow at 150°C for 30 min., 200°C for 15 min. Then, the imidised polyimide was obtained



Scheme 3.2 Synthesis path of polyimide and imidisation process.

3.2.3 Blend preparation

The powders of doped polyaniline and polyimide were blended by a dry mixing method. Both PANI and PI were grinded by using a ball-mill and filtered by sieve number 53 μm . PI:PANI composites were prepared at the weight by weight ratios of 80:20, 70:30, 50:50, 30:70, 20:80, 10:90 and 1:99.

3.2.4 Characterization

3.2.4.1 *Fourier-transform infrared spectrometer (FT-IR)*

Infrared spectra were recorded using a FT-IR spectrometer (Bruker, FRA 106/S) in the wavenumber range of 400-4000 cm^{-1} using the absorbance mode with 32 scans with the wavenumber resolution of $\pm 4 \text{ cm}^{-1}$. The KBr technique was used to prepare the powder samples .

Specimens of the synthesized undoped, doped polyaniline, doped polyaniline/polyimide blend, exposed polyaniline, synthesized polyimide and exposed polyaniline/polyimide blend in powder form at each N_a/N_{EB} ratio were prepared by grinding the specimen powder with the KBr powder. The mixture was molded in special dies under the pressure of 8 tons. The sample spectrum was recorded by using KBr as a background.

FT-IR was used to identify the characteristic functional groups of the samples in order compare with those in the literature.

3.2.4.2 UV-visible spectrophotometer (UV-visible)

UV-visible spectra were recorded with a UV-Visible spectrometer (Perkin Elmer, Lamda 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 the UV-visible spectra were recorded by using NMP as a background.

UV-visible spectrophotometer was used to investigate the electronic structure of polyaniline between undoped and doped polyaniline solution as well as the doped polyaniline/polyimide blend. The absorption spectra of the excitation of benzenoid segments, quinoid segments, bipolaron state, and polaron state were identified.

3.2.4.3 Thermogravimetric analyzer (TGA)

Thermal stability, moisture contents, and degradation process of the undoped, doped polyaniline, doped polyaniline/polyimide blend were studied by a thermalgravimetric analyzer (DuPont, model TGA 2950). The samples in powder form were weighed at 7-15 mg and then put in a titanium pan. The instrument was set to operate at temperatures from 30 to 750°C at a heating rate of 10°C/min.

3.2.4.4 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, polyaniline/polyimide blend pellet contained in a glass specimen holder and the diffraction pattern was examined between $2\theta = 5-60$ degrees.

3.2.4.5 Scanning electron microscope (SEM)

A scanning electron microscope (JEOL, model JSM-5200) was used to identify microstructures of the undoped and doped polyaniline in both pellet and powder forms. 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 stubs were coated with thin layer of gold by using a JFC-1100E ion-sputtering device. The morphology of polyaniline and polyaniline/polyimide blend was obtained by using an acceleration voltage of 25kV with a magnification of 5000 times.

3.2.4.6 Elemental analyzer (EA)

Elemental analysis (Perkin-Elmer, 2400 Series II CHS/O Analyzer) was used to determine the amount of elements in polyaniline samples. The amounts of carbon (C), hydrogen (H) and nitrogen (N_2) atoms in undoped and doped polyaniline were obtained. The doping level of the doped polyaniline film at various acid concentrations was also calculated from these amounts.

The undoped and doped powder samples were 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 a temperature between 975-1100 °C with helium as a carrier gas. The amounts of carbon (C), hydrogen (H) and nitrogen (N) were determined. The doping level of CSA and HNO_3 doped polyaniline was determined.

3.2.4.7 Differential scanning calorimeter (DSC)

Differential scanning calorimeter (Netzsch, DSC200) was used to examine the thermogram of polyimide in order to indicate its curing property. The curing temperature can be obtained from an exothermic peak.

The unimidised and imidised polyimide were weighed at 10-15 mg , sealed in Al pan, and put in the furnace. The sample was heated at 0-500 °C at a heating rate of 10 °C per minute.

3.2.5 Conductivity Measurement

3.2.5.1 *Preparation of the pellet*

0.06-0.07 g of doped polyaniline and polyaniline/polyimide blend 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 thickness was measured by using a thickness gauge; the pellet thickness varied between 0.01-0.02 mm.

3.2.5.2 *Conductivity measurement*

Electrical conductivity is the inversion of specific resistivity (ρ) which indicates the ability of material to transport electrical charge. The meter consists of four probes, which contact on a surface of film sample. Two inner probes were connected to a voltmeter for recording a change in voltage , while the outer two probes were connected to a constant current source. The voltage change was converted to the electrical conductivity of polymer using equation (1) as follow:

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

where

σ = specific conductivity (S/cm)

ρ = specific resistivity (Ω .cm)

R_s = sheet resistivity (Ω)

I = applied current (A)

K = geometric correction factor

V = voltage drop (V)

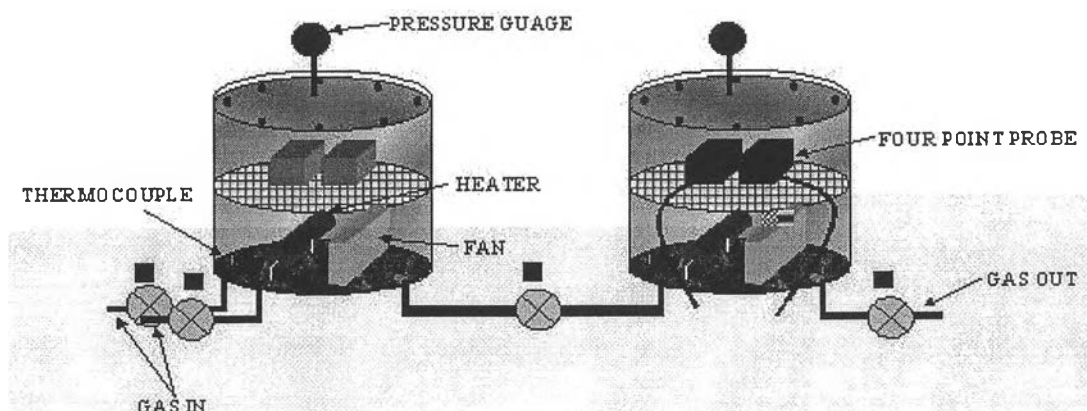
t = pellet thickness (cm)

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 resistivities were known. In our case, the sheet resistivity was measured by using the four-point probe and then the geometric correction factor was computed by equation (2) as follow:

$$K = \frac{\rho_{\text{ref}}}{R_s \times t} \quad (2)$$

where ρ_{ref} = known resistivity calibrated from the 4-point probe device at KMITL ($\Omega \cdot \text{cm}$)
 t = film thickness (cm)

Measurements of conductivity responses of doped polyaniline and polyaniline/polyimide blend 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 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 chambers.



Scheme 3.3 Conductivity detectors with gas chamber.

Step 1 A current was applied to polyaniline 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 were closed, valve No. 3 and 4 were opened).

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

Step 4 N₂ gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 5 Valve No. 3 was opened; the conductivity response of N₂ gas was recorded.

Step 6 Repeat step 2-6 until the conductivity response of N₂ was constant (this refers to preexposed $\sigma_{N_2,preex.}$).

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

Step 8 Carbon monoxide gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 9 Valve No. 3 was opened; the conductivity response of CO gas at 1000 ppm was recorded until it reached an equilibrium value.

Step 10 Valve No. 3 was closed; second chamber was evacuated by using a vacuum pump. Then N₂ gas was fed to first chamber until the pressure reached 2 atm.

Step 11 Valve No. 3 was opened; the conductivity response of CO gas at 500 ppm was recorded until it reached an equilibrium value.

Step 12 Repeat step 10 and 11 so that the conductivity responses of CO at 250, 125, 62.5, 31.25, 15.62, 7.81 and 3.90 ppm were recorded.

Step 13 Both chambers were closed and evacuated by using a vacuum pump in order to remove gas.

Step 14 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed.

Step 15 N₂ gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 16 Valve No. 3 was opened then the conductivity response of N₂ gas was 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) following;

$$\Delta\sigma = \sigma_{CO} - \sigma_{N_2,final} \quad (3)$$

where $\Delta\sigma$ = the difference in specific conductivity (S/cm)
 $\sigma_{N_2,final}$ = the specific conductivity of N₂ at final (S/cm)
 σ_{CO} = the specific conductivity of CO (S/cm).