

CHAPTER III EXPERIMENTAL

3.1 Materials

Aniline monomer (Aldrich) was used as a monomer. Ammonium peroxydisulphate (Merck) was used as an oxidant without further purification. Analytical grade hydrochloric acid (37% HCl, Aldrich) and maleic acid (98%MA, Fluka) was used as the dopants. Ammonia solution (25%, ACS reagent grade) and methanol was purchased from the Aldrich Chemical Co. Zeolites 3A, 4A, and 5A (powder, undried) were purchased from Aldrich Chemical Co. Nitrogen gas (N₂ 99% purity, TIG) was used as the carrier gas. Carbon monoxide (CO, TIG) stock was a mixture with nitrogen at 1000 ppm.

3.2 Methodology

3.2.1 Purification of Aniline Monomer

Aniline monomer was stored at 8-10°C and purified by distillation under vacuum at 60-62°C. Colorless aniline monomers were obtained and stored at 5°C prior to use.

3.2.2 Synthesis of Polyaniline Base

In this work, we followed the chemical synthesis procedure of MacDiarmid *et al.* (MacDiarmid, 1986). 7.67 grams of aniline (0.082 mole) were mixed with 89.06 ml in a 1 M HCl aqueous solution. The solution mixture was cooled at 0°C for 1 h and 98.44 ml of ammonium peroxydisulfate in 1 M HCl solution was added dropwise. Polymerization was carried out at 0°C for 3 h. The mixture color changed from clear through a blue to a dark green. The precipitated polyaniline was filtered and then washed with methanol:water (20:80) until the filtrate was completely colorless. To study the effect of doping level, the precipitated polyaniline (emeraldine salt form, ES) was converted to the emeraldine base form

(EB) by treatment with aqueous 0.1 M ammonium hydroxide solution for 4 h. The polyaniline base form was washed with methanol:water (20:80) solution and dried in vacuum oven for 48 h. Finally, the emeraldine base powder was ground with a ball mill for 3 h and sieved with mesh (53 μ m) prior to further use.

3.2.3 Preparation of Doped Polyaniline Powder

3.2.3.1 *Hydrogen chloride-doped polyaniline (PANI-HCl)*

Powder of the emeraldine base (EB) was doped and converted into the emeraldine salt (ES) at various mole ratios of an acid dopant and EB; they were 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0. EB powder was weighted at 0.724 g and immersed in the 1 M HCl solution at particular volumes of 0.4, 1.0, 2.0, 4.0, 10.0, 20.0, and 40.0 ml, respectively. The mixture was then stirred and allowed to reach equilibrium within a period of more than 48 h. The ES powder (PANI-HCl) was filtered and then vacuum-dried at 60°C for 48 h to eliminate moisture (Li and Wan, 1999).

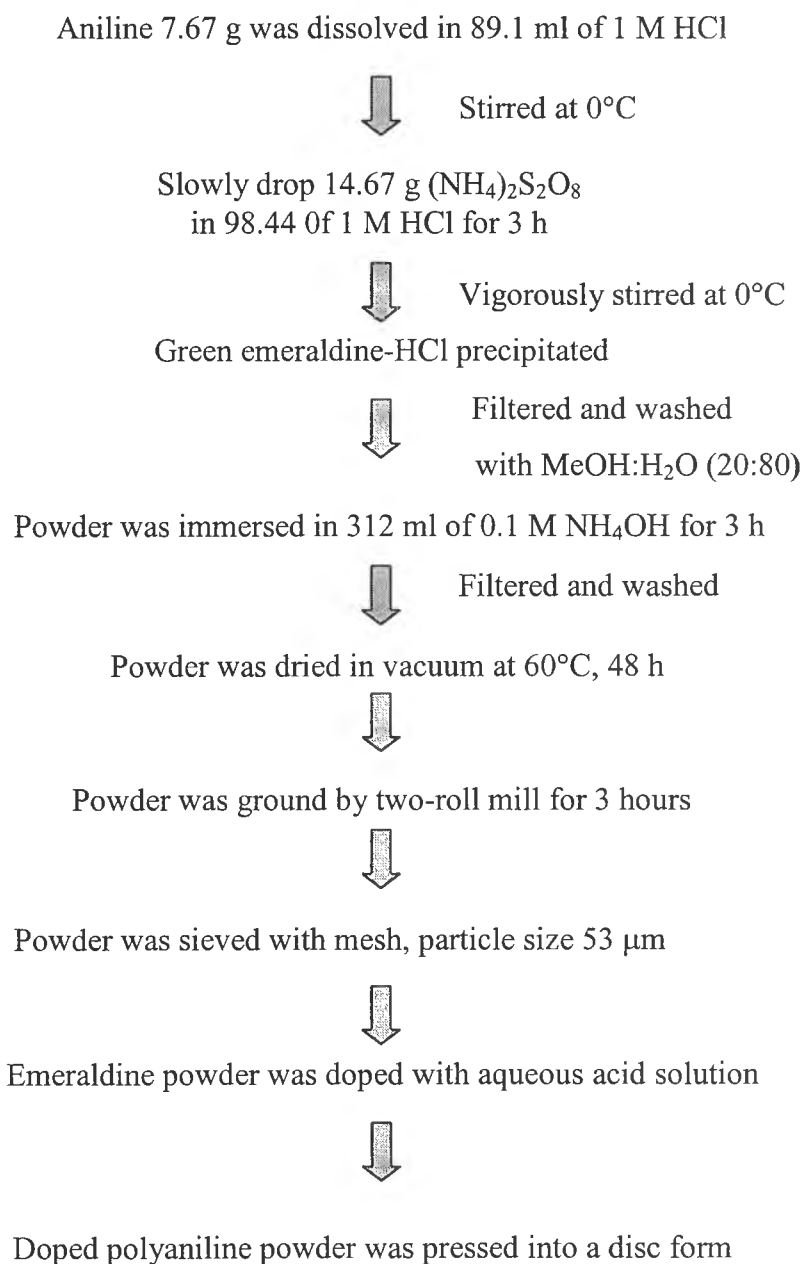
3.2.3.2 *Maleic acid-doped polyaniline (PANI-MA)*

In order to obtain maleic acid-doped polyaniline with the same mole ratios as hydrogen chloride acid doped. The volumes of 1 M maleic acid solutions used were the same as those of hydrogen chloride acid solutions, which were added to 0.724 g of emeraldine base. The mixture was then stirred and allowed to reach equilibrium during a period of 48 h. The doped powder was filtered and dried at 60°C for 48 h in a vacuum oven.

3.2.4 Preparation of Doped Polyaniline Pellet

0.075 \pm 0.002 g of doped polyaniline powder was pressed into a disc form under the pressure between 3-4 tons by a Graseby Specac hydraulic press using a stainless steel die of 2.5 cm-diameter. The pellets, having a diameter of 2.5 cm and a thickness of about 0.01 mm, were obtained. All samples were stored in a dessicator for later use.

Flow Chart of Chemical Synthesis.



3.2.5 Composite Preparation

Polyaniline/Zeolite A composites were obtained by dry mixing. Polyaniline used as the major phase was ground together with zeolite 4A. Zeolite 4A powder was dried at 120°C prior to further used. Because polyaniline was used as the major phase, a high weight fraction of zeolite 4A powder approximately 50-wt% was varied by this method to study the effect of zeolite content. To study the effect of zeolite type, zeolite 4A was replaced with zeolites 3A and 5A at 20-wt% in the polyaniline matrix.

3.2.6 Characterization

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

FT-IR spectra of the polyaniline sample were taken with a Bruker, modal EQUINOX55/S spectrometer in the absorption mode with 32 scans at a resolution of 4 cm^{-1} . The wavenumber range observed was 400-4000 cm^{-1} . The samples were prepared by grinding the powdered polyaniline with the KBr powder. The mixture was molded in special dies under the pressure of 8 tons into a pellet. The sample spectra were recorded by using KBr as a background. In situ FT-IR technique was used to investigate the CO interaction of acid-doped polyaniline exposed to a CO/N₂ mixture. The sample of acid-doped polyaniline/KBr pellet was placed in the holder of the gas cell. At that instance, the sample spectrum was taken as the background. Then the sample was exposed to a 1000 ppm CO/N₂ mixture, and a FT-IR spectrum was recorded every 10 minutes.

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

3.2.6.2 *UV-visible spectrophotometer*

UV-visible spectra were recorded with a Perkin Elmer, model Lamda 10 spectrometer in the wavelength range of 290-900 nm. To investigate the electronic structure of polyaniline, samples were prepared by dissolving in NMP at a concentration of 0.05 g/l. Each sample was put in a quartz cell and recorded the UV-visible spectra by using NMP as the background.

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

3.2.6.3 Scanning electron microscope (SEM)

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology and surface appearance of PANI powder and pellet form and identify morphology of zeolite powder. A piece of sample was placed on the holder with an adhesive tape and coated with a layer of gold by using a JFC-1100E ion-sputtering device before measurements taken. The scanning electron micrographs of polyaniline were obtained by using an acceleration voltage of 25 kV with a magnification of 1000-3500 times.

3.2.6.4 Thermogravimetric analyzer (TGA)

The moisture contents of polyaniline and zeolite were studied by a DuPont model TGA 2950 thermalgravimetric analyzer. Each sample was weighed at 10-15 mg and then put in an aluminum pan. The instrument was set to operate at temperatures from 30 to 700°C at a heating rate of 10°C/min.

3.2.6.5 Elemental analyzer (EA)

Elemental analysis was used to determine the contents of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) atoms of the undoped and doped polyanilines. The ratio of H/N indicated the doping levels of the acid-doped polyaniline. Elemental analysis data were taken with a Perkin-Elmer PE2400 Series II Elemental Analyzer in the CHNS/O mode at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

3.2.6.6 X-ray diffraction spectroscopy (XRD)

An X-ray diffractometer (Rigaku model) was used to investigate orderly arrangements of atoms or molecules and to determine the crystal structures of undoped polyaniline, acid-doped polyaniline and zeolite samples. X-ray diffraction patterns were recorded on a Phillips PW 1830/00 No. DY 1241 diffractometer. Each XRD sample of polyaniline was measured in a pellet form

contained in an aluminum specimen holder and the diffraction pattern was examined between $2\theta = 5-50$ degrees.

3.2.6.7 Particle size analyzer

The particle sizes of polyaniline and zeolite samples were determined by using a Masterizer X Version 2.15 particle size analyzer, (Malvern Instruments Ltd.). The lenses used in this experiment were 45 and 300 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

3.2.7 Conductivity Measurement: Four-point Probe Meter

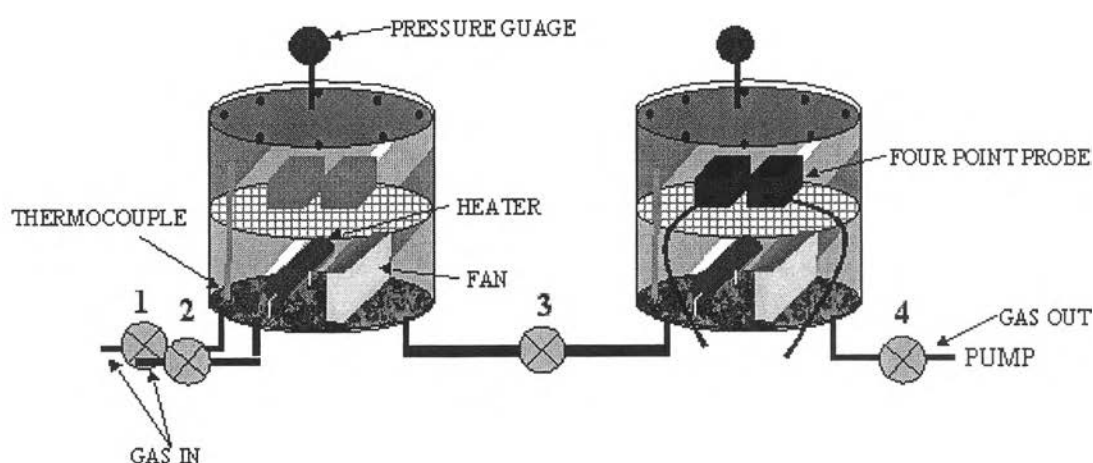
Electric conductivity, σ (S/cm) is the inversion of specific resistivity ρ ($\Omega \cdot \text{cm}$), which indicates the ability of electrical charge transportation. This meter consisted of four probes, the inner two probes was connected to a voltmeter for detecting the voltage drop, while the outer two probes was connected to a constant current source. The voltage drop measured was converted to the electrical conductivity of polymer by using equation as follows:

$$\sigma = (1/\rho) = (1/Rt)(1/K) \quad (3.1)$$

where R is the sheet resistivity (Ω), t is the pellet thickness (cm.) and K is the geometric correction factor. The geometric correction factor K was taken into account of the geometric effect, depending on the configuration and probe tip spacing and K was determined by using standard materials whose specific resistivity values were known. In this case, the sheet resistivity was measured with a custom-built four-point probe (Prissanaroon, 2001) and then the geometric correction factor was computed from the equation: $K = \rho_{\text{ref}} / (R_s t)$ where ρ_{ref} is known resistivity and t = film thickness (cm.). The specific conductivity was measured in 1 atm of N_2 at $27 \pm 1^\circ\text{C}$ in the linear Ohmic regime, and the DC current used between 15-20 mA as shown in Appendix I-J.

3.2.8 Gas Measurement

Measurements of conductivity responses of doped PANI and PANI/Zeolite composite were carried out by using a special constructed gas cell. It consisted of two chambers connected in series. The chambers were made from stainless steel. 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. The procedure for measuring the electrical conductivity in the presence of a carbon monoxide gas (CO) was as follows. With a fixed voltage applied to the sample, pure nitrogen was passed through the sample chamber until a steady conductivity value was obtained. The nitrogen was turned off and the chamber was then vacuumed. The 1000-ppm CO gas mixture was let in and the conductivity was recorded after reaching equilibrium. The CO gas was then turned off and the chamber was then vacuumed and the next lowest concentration was admitted to the chamber by dilution with nitrogen. The procedure was repeated until no significant change was observed. The changes in conductivity ($\Delta\sigma = \sigma_{\text{CO}} - \sigma_{\text{Final N}_2}$) observed were for the CO concentrations of 1000, 500, 250, 125, 62.5, 31.25, 15.63, and 7.86 ppm for both the PANI and PANI/Zeolite samples.



Scheme 3.1 Conductivity detectors with gas chamber