CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

Pyrrole monomer, obtained from Sigma, was stored at 8 - 10 $^{\circ}$C and dried with CaH_2 (Fluka) for 24 hours before use. Ammonium persulfate, APS was obtained from BDH Laboratory Supplies as an oxidant. Dodecylbenzene sulfonic acid (DBSA) was obtained from Sigma as dopant and was used as received. Since DBSA is sensitive to humidity, it was stored in a dry place.

m-Cresol obtained from Merck was used as solvent to make polypyrrole solution for studying UV-VIS spectra and casting polypyrrole films .

Sulfurdioxide balanced with nitrogen obtained from TIG was the toxic gas studied in this work. The stock tank concentration was 2500 ppm. Properties, toxicity data of SO_2 are shown in Appendix A.

2.2 Methodology

2.2.1 Synthesis of DBSA-doped polypyrrole

In this work, polypyrrole was synthesized following the method of *Lee et al. (1995)*. This method is the chemical polymerization of polypyrrole soluble in organic solvent and electrically conductive in dried state and is shown in Figure 2.1.
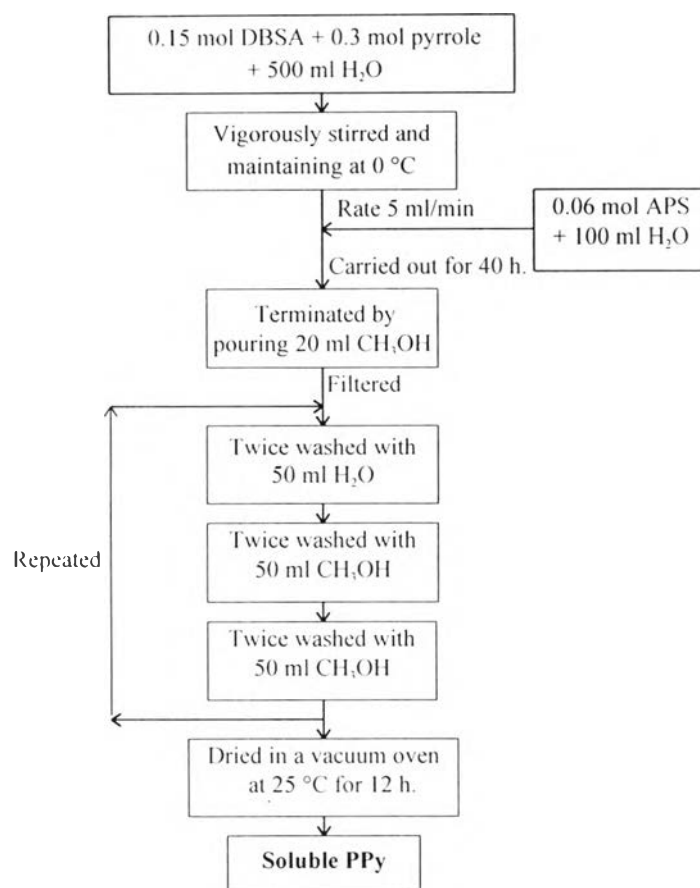
Figure 2.1   Flow chart of synthesis of soluble polypyrrole.

Pyrrole monomer was dried by mixing pyrrole monomer with CaH_2 in the ratio of 100 g of CaH_2/L of pyrrole and this reaction was kept for 24 hours before used. 0.3 mole of dried pyrrole monomer and 0.15 mole of DBSA were dissolved in 500 ml of distilled water. This mixture was maintained at about 0 °C and vigorous stirred for 5 minutes. A 0.06 mol of APS in 100 ml of distilled water was slowly added to the above solution with a rate of 5 ml/minute as shown in Figure 2.2. Reaction was carried out for 40 hours and then terminated by pouring in 20 ml of methanol. The resultant polypyrrole powder was filtered and washed sequentially twice with 50 ml distilled water, 50 ml methanol and 50 ml acetone. The washing part was repeated and followed by filtering and drying in vacuum oven at 25 °C for 12 hours.

Polypyrrole powder was stored in a dessicator. The product was characterized by FTIR, EA, SEM, UV-VIS, and conductivity detector.

To study the effect of doping level on the conductivity response of polypyrrole films, polypyrrole was synthesized in the same method but the amount of DBSA used was varied from 0.15, 0.20, 0.25, 0.30, 0.35, 0.40 and 0.45 mole/L.
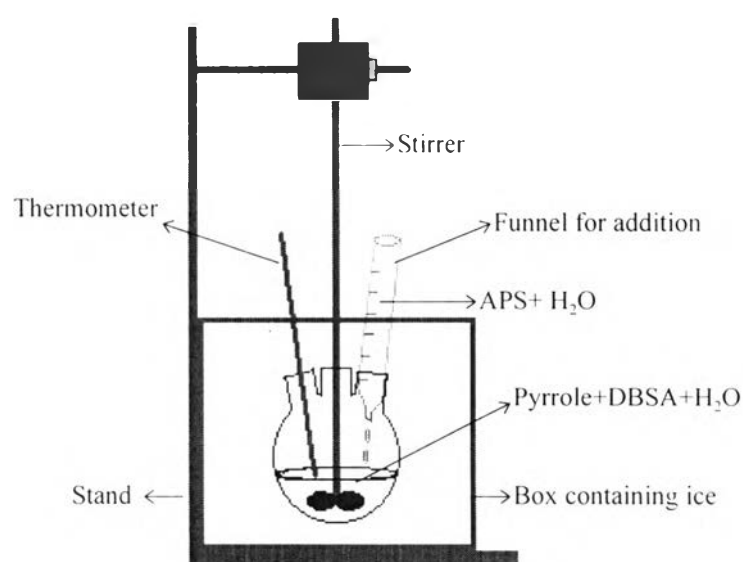

Figure 2.2 A scheme of the apparatus for synthesis DBSA-doped polypyrrole.

2.2.2   Preparation of DBSA-doped polypyrrole films

1 gram of DBSA-doped polypyrrole synthesized as mentioned in the section 2.2.1 was completely dissolved by ultrasonification in 25 ml of m-cresol at room temperature for 60 minutes. DBSA-doped polypyrrole solution was filtered through a 1 μm Teflon membrane filter. 1 ml of the solution was cast onto a glass slide by using a glass syringe and the solvent was dried at 210 °C for 5 hours. The resulting DBSA-doped polypyrrole film was stored in a dessicator before use.

2.3 Characterization / Sample Preparation

2.3.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra were obtained on a FT-45 A Bio-Rad Spectrometer in order to characterize the important functional groups of the synthesized DBSA-doped polypyrrole. The FTIR experiment was done in a transmission mode with 16 scans at a resolution of 8 cm^{-1}. A frequency range of 4000 - 400 cm^{-1} was observed using a deuterated triglycine sulfate detector (DTGS) with a specific detectivity, D*, of 1×10^4cm.Hz$^{1/2}$ W^{-1}.

Optical grade KBr commercially avialable from CarloErba Reagent was used as background. The KBr was pressed hydraulically into a pellet and quickly taken to the FT-IR chamber. The KBr spectra background was collected with 16 scans. After obtaining the background spectra, the sample was then mixed with dried KBr at an approximate ratio of 1:20 = sample:KBr, using the KBr sample used in the background spectrum. The solid mixture was ground and transferred to the sample holder using the same procedure as mentioned above.

2.3.2 Elemental Analyzer (EA)

The doping level of the resulting polypyrrole was determined from the S/N ratio, monitored by Perkin-Elmer 2400 Series II Elemental Analyzer in CHNS mode. C, H, N, and S can be determined simultaneously with analysis times ranging from 6 to 14 minutes. He (20 psi) and O$_2$ (15 psi) were used as the carrier gas and the combustion gas, respectively.

DBSA-doped polypyrrole powder was weighed in at 2 mg and sealed in disposable tin capsules and placed in a 49-position sample carousel. Polypyrrole was flushed with He and dropped into the combustion tube where it was burnt at 975 °C for about 3 minutes. Added heat from the oxidation of

the tin increased the temperature to above 1800 ^{o}C for a complete combustion. To obtain quantitative oxidation, the combustion products were transferred with He carrier gas over efficient oxidation catalysts and flushed into the reduction tube filled with reduced Cu. Oxide of N was converted to elemental N at temperatures between 550 ^{o}C and 700 ^{o}C, while interfering components, S, was removed from the gas mixture with Pb chromate and Ag wool.

The doping level of the resulting DBSA-doped polypyrrole was calculated from the S/N weight ratio by using Equation 2.1 :

$$\% \text{ Doping level} = \frac{S}{N} \times \frac{M_N}{M_S} \times 100 \qquad (2.1)$$

where

S	=	mass of S from Elemental Analyzer (g)
N	=	mass of N from Elemental Analyzer (g)
M_N	=	molecular weigh of N
M_S	=	molecular weigh of S

2.3.3 Scanning Electron Microscope (SEM)

Scanning electron micrographs were taken out to determine the thickness of the polypyrrole film and to observe the film morphology. SEM digitized photographs were obtained from JOEL 5200 - 2AE (MP 1515200), with a magnification range of 35 - 200,000 times.

DBSA-doped polypyrrole film prepared as mentioned in the section 2.2.2 was cut into 0.2 cm to 0.5 cm. A piece of film was attached to a brass-stub by using adhesive tape and then the surface of the sample was coated with the thin Au film produced by a vacuum evaporation. The sample was placed into the specimen stage inside the microscope. The pictures were collected by using an acceleration voltage of 15 kV with magnification 750 -

1000 times. The film thickness was measured from an edge view of the sample by using standard scale setting in the SEM program.

2.3.4 Ultraviolet-Visible Spectrometer (UV-VIS)

The ultraviolet-visible spectra were recorded with a Perkin-Elmer instrument Spectrometer Lambda 16 in order to observe the polaron and bipolaron absorption of conductive polymers. A Deuterium lamp was used as the light source. m-Cresol was used as the solvent. The sample solution was prepared by dissolving 0.05 g of DBSA-doped polypyrrole with 100 ml of m-cresol in the ultrasonic bath for 60 minutes and then filtering through a 1 µm Teflon membrane filter. The sample solution was viewed microscopically for centering and aperturing to a particular area. The transmission light then passes to a dispersive system to record the light transmission as a function of wavelength in the range of 190 - 800 nm.

Because the polaron and bipolaron absorption are frequently considered in electron volt unit. the absorption wavelength was converted to photon energy by using Einstein's equation as shown in Equation 2.2 :

$$E = h\nu = \frac{hc}{\lambda} \tag{2.2}$$

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)

the photon energy in J can be converted to electron volt by dividing with 1.602 $\times 10^{-19}$ J/eV.

2.4 Electrical Properties

2.4.1 The Four-Point Probe for Characterizing Sheet Resistivity

The four-point probe is commonly used to measure the sheet resistivity of thin layers or thin films. A four-point metal-tip probe assembly is lightly press into the surface as shown in Figure 2.3. Probe tip spacings typically range from 0.025 inches to 0.062 inches. The sheet resistance is obtained by introducing a current (I) through outer two pins and determining the voltage drop (V) across the inner two pins. The sheet resistance is calculated from Equation 2.3 :
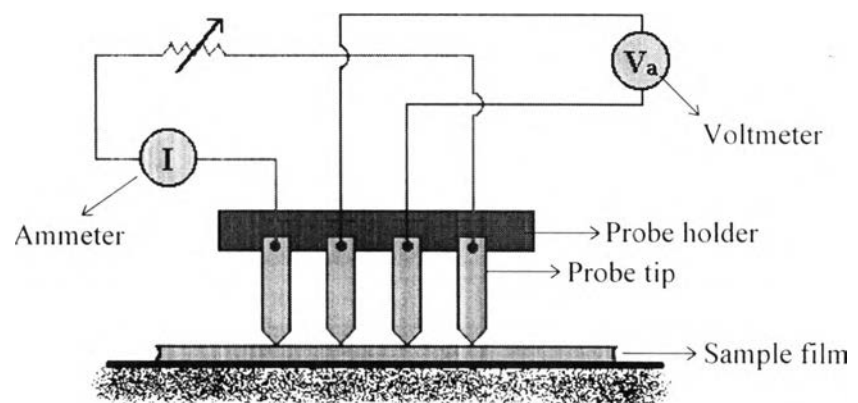

Figure 2.3 **Scheme of the four-point probe. A typical spacing is 1 mm between probes.**

$$R_s = K \times \frac{V_a}{I} \tag{2.3}$$

where

R_S =   sheet resistivity (Ω)

K   =   Geometric correction factor

V_a =   voltage drop (V)

I   =   applied current (A)

The Geometric correction factor takes into account geometric effects. It depends on the configuration and probe tip spacing and can be determined by using standard materials whose specific resistivities are known (Appendix B). Sheet resistivity of these material was measured by using the four-point probe detector and then the geometric correction factor was computed from Equation 2.4 :

$$K = \frac{\rho_{ref}}{R_s \times t} \tag{2.4}$$

where

ρ_{ref} =   known resistivity from the chemical handbook (Ω.cm)

t   =   film thickness (cm)

So the specific conductivity of a polypyrrole film with known thickness can be calculated from Equation 2.5 :

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{1}{K \times V_a \times t} \tag{2.5}$$

where

σ = specific conductivity (S/cm)

ρ = specific resistivity (Ω.cm)

I = applied current (A)

K = Geometric correction factor

V_a = voltage drop (V)

t = film thickness (cm)

2.4.2 Conductivity Detector With Gas Chamber

2.4.2.1 Construction. Measurements of conductivity responses of the polypyrrole films to SO_2 were recorded using a specially-constructed gas-sensitivity cell. A schematic representation of the apparatus is shown in Figure 2.4. It consisted of two chambers of $8\times8\times8$ inch^3 connected in series. The chambers were made from Stainless Steel No.316, size 3 mm with high corrosion resistivity. The first chamber consisted of four 5×8 inch^2 buffles for a uniform gas mixing and a finned heater for controlling the testing temperature of polypyrrole films. This chamber was connected to two Perkin-Elmer Flow meters No. 62-01 with stainless steel floats for controlling various SO_2 concentration. The second chamber contained the sample holder and four-metal tip probes for conductivity measurement based on the four-point probe theory. A pressure gage was connected to this chamber for controlling the testing pressure. The temperature controller from Shinho, Digital DCN 720 connected to both chambers with a thermocouple was used to monitor and control temperatures within the chambers.

2.4.2.2 Operation. DBSA-doped polypyrrole film was located on the sample holder and pressed by four probes of conductivity detector system in the second chamber. The operation can be divided into 3 steps ;

- Step 1 : Valve no. 1 and no. 2 were opened while valve no. 3 was closed. Both chambers were evacuated by using a vacuum pump.

- Step 2 : Valve no. 1 was closed and then N_2 that served as the carrier gas and SO_2 were fed into the first chamber already set at the desired temperature. N_2 and SO_2 flows were controlled by a regulator from Air Products and flow rates of both gases were calibrated by measuring the volume of gas passing through the system per unit time using Perkin-Elmer Flow meter. When the feeding step was finished the pressure in the first chamber became 2 atm as observed from pressure gage No.1. To get a good uniformly mixed gas, this gas mixture was maintained for 5 minutes in the first chamber after finishing the feeding step.

- Step 3 : The current was applied to the polypyrrole film and then the gas mixture was allowed to be exposed to the second chamber by opening the ball valve No.1. The pressure of each chamber equilibrated to 1 atm. The voltage drop was detected at 30 minutes after starting exposure of gas to polypyrrole film when the response became saturated. The specific conductivity can be calculated by using Equation 2.5.

2.4.2.3 Calculation of Flow rate and Feeding time for various SO₂ concentration. The calculation part can be divided into 3 steps ;

- Step 1 : Determination of mole of gas mixture

  From Dalton's law ;

$$P_m = P_a + P_b + P_c$$

where

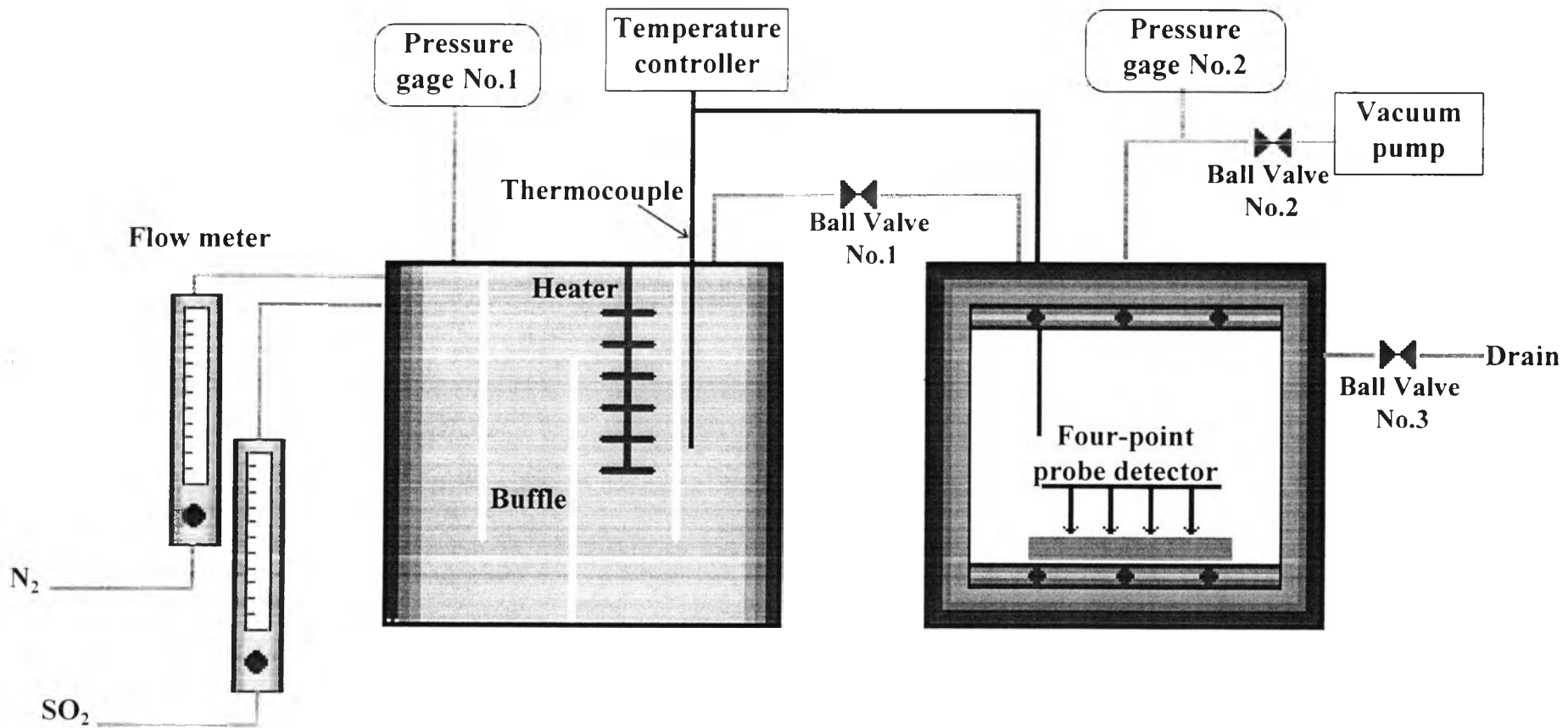|		
P_m	=	total pressure of mixed gas
P_a, P_b, P_c	=	partial pressure of gas a, b, c respectively

and

$$PV = nRT$$

Figure 2.4   A schematic representation of conductivity detector with gas chamber.

therefore.

$$P_m = (n_a + n_b + n_c) \frac{RT_m}{V_m}$$

and then,

$$P_m = (n_m) \frac{RT_m}{V_m}$$

where

P_m	=	total pressure of mixed gas (atm)
n_m	=	mole of gas mixture (mole)
R	=	Gas constant = 82.057 atm.cm^3/mol.K
T_m	=	temperature of gas mixture (K)
V_m	=	volume of gas mixture (cm^3)
	=	volume of two chambers (cm^3)

In calculation of flow rate and feeding time for various SO_2 concentration. the mole of gas mixture was first calculated from Equation 2.6

$$n_m = \frac{P_m \times V_m}{R \times T_m} \tag{2.6}$$

• Step 2 : Determination of the desired mole of stock SO_2 and N_2 for obtaining the certain gas concentration. The mole of pure SO_2 needed for each concentration was calculated by using Equation 2.7 :

$$n_{SO_2} = \frac{c_{SO_2}}{10^6} \times n_m \tag{2.7}$$

where

n_{SO_2} = the desired mole of pure SO_2 (mol)

c_{SO_2} = the desired SO_2 concentration (ppm)

n_m = mole of gas mixture (mole)

Because stock SO_2 concentration was 2500 ppm (0.25 %), so the wanted mole of stock SO_2 (n_{stock}) can be calculated from

$$n_{stock} = \frac{100}{0.25} \times n_{SO_2} \tag{2.8}$$

and the mole of N_2 needed to mix with stock SO_2 (n_{N_2}) is

$$n_{N_2} = n_m - n_{stock} \tag{2.9}$$

● Step 3 : Determination flow rate and feeding time of stock SO_2 and N_2. First we had to convert the amount of stock SO_2 and N_2 from mole to volume because cubic meters were used in detecting the volume flow rates of stock SO_2 and N_2

$$V_{stock} = \frac{n_{stock} \times M_{SO_2}}{\rho_{SO_2}} \tag{2.10}$$

and

$$V_{N_2} = \frac{n_{N_2} \times M_{N_2}}{\rho_{N_2}} \tag{2.11}$$

where

V_{stock}, V_{N_2} = the desired volume of stock SO_2 and N_2, respectively (cm^3)

n_{stock}, n_{N_2} = the desired mole of stock SO_2 and N_2, respectively (mol)

M_{SO_2}, M_{N_2} = molecular weight of SO_2 and N_2, respectively (g/mol)

ρ_{SO_2}, ρ_{N_2} = density of SO_2 and N_2, respectively (g/cm^3)

From the calibration data of flow meter no. 62-01, we used the flow rate at 730 cm^3/min, so feeding time of both gases can be calculated from

$$t = \frac{V}{730} \tag{2.12}$$

where

t	=	the feeding time of gas (min)
V	=	the desired volume of gas (cm^3)