



CHAPTER III EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

Diphenylamine (ACS reagent, Sigma Aldrich) was used to monomer. Ammonium persulfate (AR grade, Riedel-de Haën) and 36.5-38% Hydrochloric acid (ACS reagent, J.T. Baker) were used as oxidant and catalyst, respectively. Polyethylene oxide (AR grade, ACROS organics), which had molecular weight 600,000, was used to improved processibility in melt-spinning method. Ammonium hydroxide solution (AR grade, Panreac), Toluene (AR grade, Panreac), Isopropyl alcohol (AR grade, Burdick & Jackson), Ethanol (AR grade, Lab Scan), Methanol (AR grade, Lab Scan) Dichloromethane (AR grade, Lab Scan) were used without purification.

3.1.2 Instruments

A Fourier transform infrared spectrometer, FT-IR (Thermo Nicolet, Nexus 670) was used to characterized the functional groups of PDPA. The thermogravimetric analyzer (Perkin Elmer, TGA7) was used to determine the thermal behavior of polymers. The particle sizes of De-PDPA were determined by using the particle size analyzer (Masterizer X). The XRD pattern of De-PDPA and D-PDPA at various doping mole ratios (1:1, 10:1, 100:1, 200:1) were recorded on a X-ray diffractometer (Rigaku D/MAX 2200). The morphology and size of PDPA electrospun nanofibers were investigated by using scanning electron microscope, SEM (JEOL, model JSM-5410LV).

3.2 Experimental

3.2.1 Synthesis of Polydiphenylamine (PDPA)

PDPA was synthesized via the interfacial polymerization (Orlov *et al.*, 2006). A 0.2 M solution of diphenylamine in toluene, and a 0.25 M solution of ammonium persulfate ((NH₄)₂S₂O₈) in distilled water of the same volume as a 1 M

solution of hydrochloric acid (HCl) were prepared. The solutions of the monomer and the oxidizer were first cooled to temperature between -2 and 0 °C and then mixed momentarily. The reaction was carried out under a continuous intense stirring for 4 h where the temperature of the reaction mixture was maintained at the between -2 and 0 °C. At a certain time interval, the reaction mixture was precipitated into a 5-fold excess of isopropyl alcohol having a green color; filtered, and the mixture was washed many times with distilled water until the reaction was neutral (colorless).

3.2.2 Neutralization of PDPA

HCl-doped PDPA (1.8 g), 5 mL of ethanol, and 20 mL of 1 N NH_4OH solution were mixed with intensive stirring. The neutralization was taken place at room temperature, 27 °C, for 24 h. The neutralized PDPA was washed a few times with ethanol/water mixtures (3/1, v/v) until no colored supernatant was observed. The dark purple PDPA particles were dried under vacuum at room temperature for at least 24 h (Hua *et al.*, 2003).

3.2.3 Doping of PDPA

The PDPA was doped with HCl solutions at room temperature, 27 °C, by precisely controlling the mole ratio between PDPA and 5M HCl solution (Hua and Ruckenstein, 2005).

3.2.4 Preparation of Electrospun Nanofibers PDPA

Firstly, PDPA was dissolved in dichloromethane (DCM). The PDPA solutions were blended with polyethylene oxide (PEO) at various concentrations; 95:5, 97:3, 98:2 %w/w. The PDPA contents in the solutions were 30% and 50%. Then solutions were stirred and processed in an ultrasonic bath to ensure homogeneous PDPA solutions. Electrospinning of the PDPA solution was performed at a flow rate of 10 mL/h with a potential difference of 10 kV. A distance between the syringe tip and the collector is 15 cm. Membranes were accumulated on the collector (drum) with an aluminium foil laid on the collecting surface (Gopalan *et al.*, 2008).

3.3 Characterization and Testing

3.3.1 Characterizations

3.3.1.1 *Fourier Transform Infrared Spectrometer*

The polymers were first characterized for the functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) in absorption mode with 32 scans and a resolution of $\pm 2 \text{ cm}^{-1}$, wavenumbers range of $4000\text{-}400 \text{ cm}^{-1}$, and using a deuterated triglycine sulfate as a detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. De-PDPA and D-PDPA were intimately mixed with dried KBr at a ratio of PDPA: KBr = 1:20.

3.3.1.2 *Thermogravimetric Analyzer*

The thermogravimetric analyzer (Perkin Elmer, TGA7) was used to determine the thermal behavior of polymers. The experiment was carried out by weighting a powder sample of 5-10 mg and placed it in a platinum pan, and then heated it under nitrogen flow with the heating rate $10 \text{ }^\circ\text{C}/\text{min}$ from $30\text{-}800^\circ\text{C}$.

3.3.1.3 *Particle Size Analyzer*

The particle sizes of De-PDPA were determined by using the particle size analyzer (Masterizer X).

3.3.1.4 *X-ray Diffractometer (XRD)*

The XRD pattern of De-PDPA and D-PDPA at various doping mole ratios (1:1, 10:1, 100:1, 200:1) were recorded on a X-ray diffractometer (Rigaku D/MAX 2200) operated at scan range $5\text{-}90$ degree, scan step 0.05 degree, scan speed $5 \text{ degree}/\text{min}$ 30MA and 40 KVP .

3.3.1.5 *Scanning Electron Microscope (SEM)*

To investigate the morphology and size of PDPA electrospun fibers by using SEM (JEOL, model JSM-5410LV).

3.3.2 Electrical Conductivity and Sensitivity Measurement

Electrical conductivity was measured by using a custom-built two-point probe. To determine the electrical conductivity, doped-PDPA was pelleted into 2.5 cm diameter circular pellets and PDPA electrospun nanofibers with different

amount of PEO were cut into a circular shape. The specific conductivity, σ (S/cm) was obtained by measuring the resistance, R , and using the following relation

$$\sigma = (1/Rt)(1/K) \quad \text{Eq. 3.1}$$

where, t is the film thickness and K is the geometric correction factor. A geometric correlation factor was calibrated by using standard silicon wafer sheets with known specific resistivity values. The measurements were performed in the linear Ohmic regime, i.e. the specific conductivity values are independent from the applied DC current. The measurements were carried out at 25°C and repeated at least three times.

Measurements of conductivity responses of doped PDPA and PDPA electrospun fibers are recorded by using a specially constructed gas cell. It consists of two chambers connected in series. The chambers are made from stainless steel. The second chamber contains two point probe meters for conductivity measurement. The temperature controllers, connecting to both chambers, are used to monitor and control the temperature within the gas chambers.

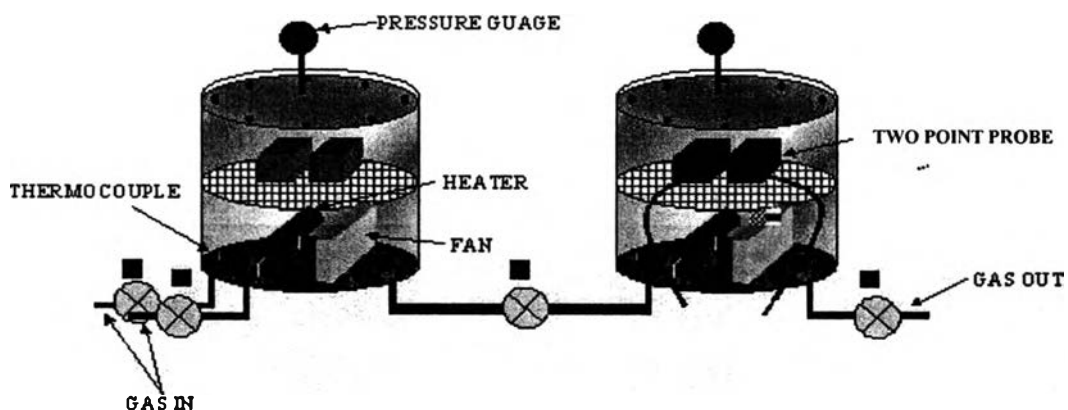


Figure 3.1 Conductivity detectors with gas chamber.

Step 1 A current is applied to PDPA pellets in order to measure conductivity before exposing to gas.

Step 2 Both chambers are 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 are opened).

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

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

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

Step 6 Steps 2-6 are repeated until the conductivity response of N₂ is constant (this refers to preexposed σ_{N_2} , preex.).

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

Step 8 methanol vapor is fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 9 Valve No. 3 is opened; the conductivity response of the vapor is recorded until it reached an equilibrium value.

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

Step 11 Both chambers are closed and evacuated by using a vacuum pump in order to remove gas.

Step 12 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) are closed.

Step 13 N₂ gas is fed into the first chamber until the pressure reaches 2 atm as observed from the pressure gauge.

Step 14 Valve No. 3 is opened then the conductivity response of N₂ gas is recorded as the final ΔN_2 , final.

The differences in the change of electrical conductivity ($\Delta\sigma$) at various doping ratios are calculated by Equation 3.2 following;

$$\Delta\sigma = \sigma_{MeiOH} - \sigma_{N_2initial} \quad \text{Eq. 3.2}$$

The sensitivity is defined as the electrical response divided by its conductivity at the final N₂ (Densakulprasert *et al.*, 2003).

$$\text{sensitivity} = \Delta\sigma / \sigma_{N_2 \text{ initial}} \quad \text{Eq. 3.3}$$