CHAPTER III

AC PLASMA SYSTEM AND EXPERIMENTAL

This chapter was divided into two parts. The first part was the AC plasma system. Our design, construction, and testing of the assembled AC reactor will be described in which the details of vacuum chamber, transformer, monomer vessel, and cold trap will be laid out and photograph of AC system. The second part described experimental details and equipment for synthesis and characterization of polypyrrole films by using plasma technique.

3.1 AC plasma system

3.1.1 The design and construction of AC plasma system

The AC plasma system was designed to be assembled as an economical locally made prototype, the lay out and photograph of the AC system are shown in **Figure 3.1** and **Figure 3.2**, respectively. The system was composed of two main parts: a plasma part and a chemical part. In the plasma part consisted of a vacuum chamber, power supply. The AC power supply transfer voltage to transformer. The transformer was increasing tenfold of voltage from power supply. Thence, there transfer to the electrodes in the chamber. Another main part comprised of monomer vessel and cold trap. Liquid monomer was contained into monomer vessel which purges nitrogen gas in order to carry monomer vapor into the chamber. The cold trap was used in conjunction with evacuation system (Edwards rotary vane pump) to collect condensation produced from residue monomer.

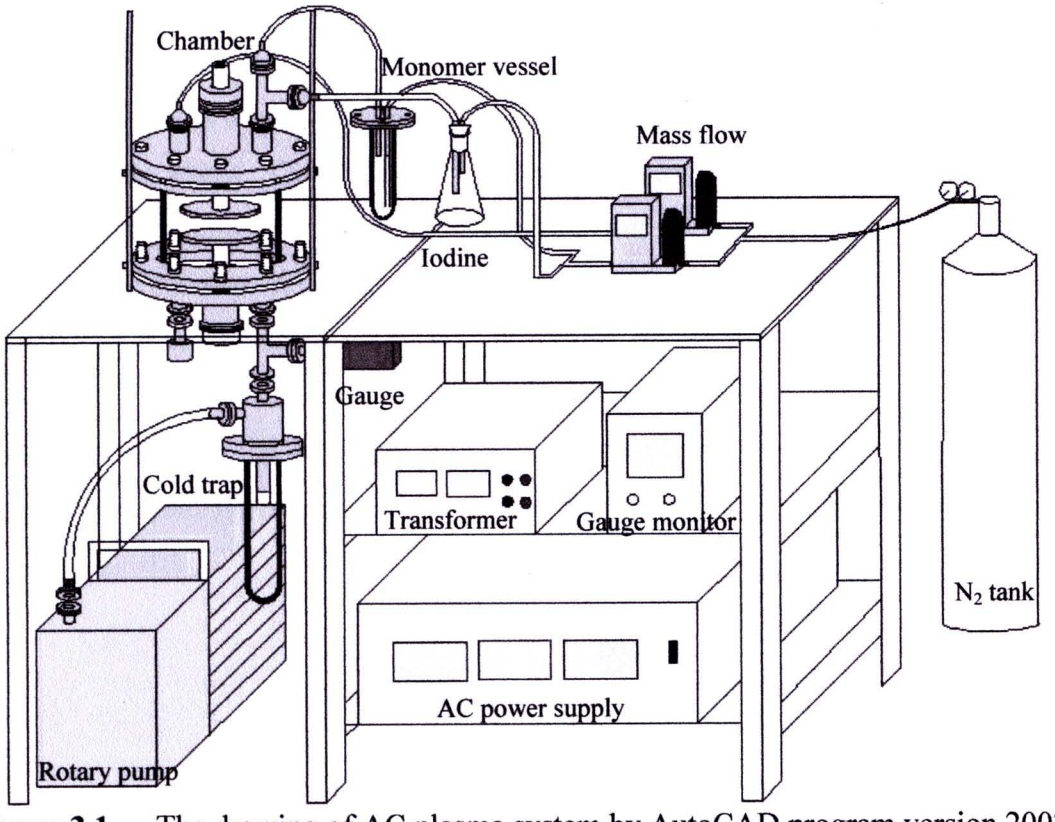


Figure 3.1 The drawing of AC plasma system by AutoCAD program version 2007.

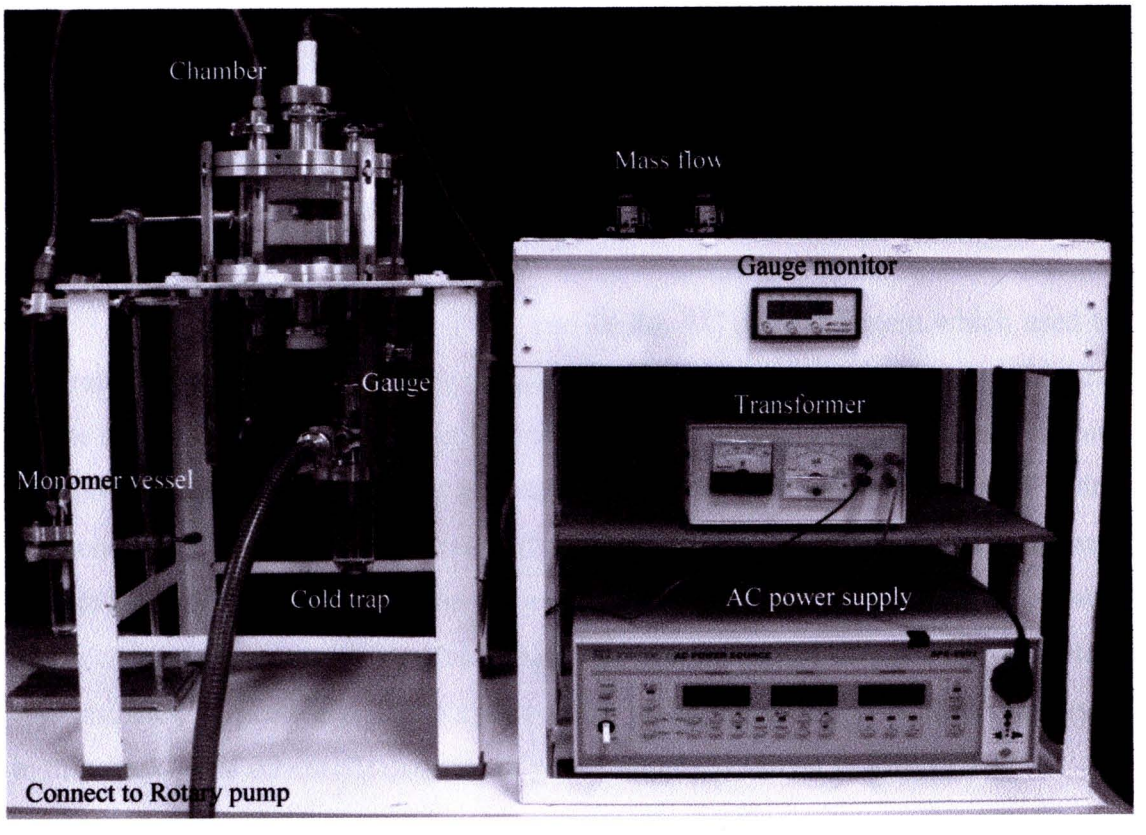
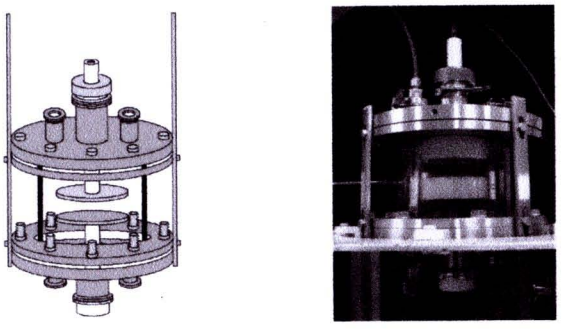


Figure 3.2 The photograph of AC plasma system.

3.1.1.1 Vacuum chamber

The system was made from a glass cylinder with both ends covered by stainless steel plates. The assembly is depicted in **Figure 3.3**. The length of glass cylinder is approximately 15 cm and has an outer diameter of 15 cm. At the center of the chamber lie two electrodes (6 cm in dimension). The distance between each electrode is about 5 cm. The electrodes were made from stainless steel. The vacuum chamber has six ports, which two ports (NW 40) was used for electrodes and four ports (NW 16) used for cold trap, leak valve, vacuum gauge and reagent feed line for gaseous reagents. The details of flanges are described clearly in **Appendix A**.



(a) AutoCAD Design (b) Chamber

Figure 3.3 (a) Schematic diagrams of vacuum chamber by AutoCAD program version 2007 and (b) photographs of the actual vacuum chamber.

3.1.1.2 Power supply

Power supply is another part of the AC plasma system which used to generate voltage and current into electrode for plasma generating. In this work, the power supply consists of two parts, AC power supply and step up transformer circuit. AC power supply was used to generate voltage in the range of 0-300 V with frequency in the range of 0-100 Hz into step up transformer circuit. This circuit was used to amplify the voltage ten times from AC power supply into the electrode, as was in the vacuum chamber. The output voltage and current can be detected by voltmeter, and ammeter, respectively. The output voltage in the range of 800- 1500 V was used in this work. The schematic diagram of power supply is shown in **Figure 3.4**.

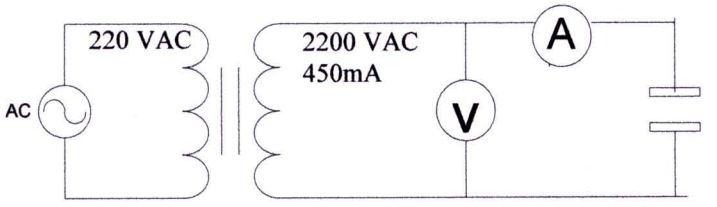
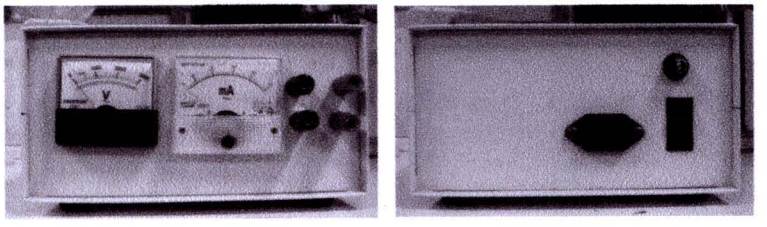


Figure 3.4 Diagram of step up circuit.



(a) Front view (b) Back view

Figure 3.5 The photograph of the transformer box.

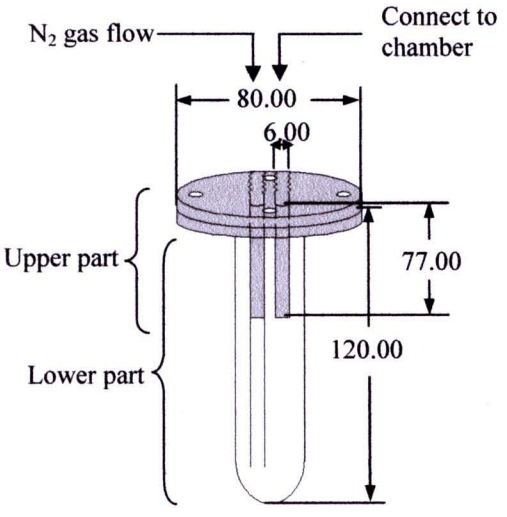
3.1.1.3 Monomer vessel

The compartments in which chemicals will be handled were composed of a monomer vessel and a cold trap **(Figures 3.6 and 3.7)**. The monomer vessel was consisted of a stainless steel plate (upper part) and borosilicate monomer container (lower part). The upper part consists of two ports (swagelok port). One port designed to intake a carrier gas feed, is connected with a nitrogen tank. And another port was designed to connect a monomer. Nitrogen as a carrier gas would be fed into the monomer container though the small inner tube in order to purge the containing monomer vapor and flow into the chamber.

3.1.1.4 Cold trap

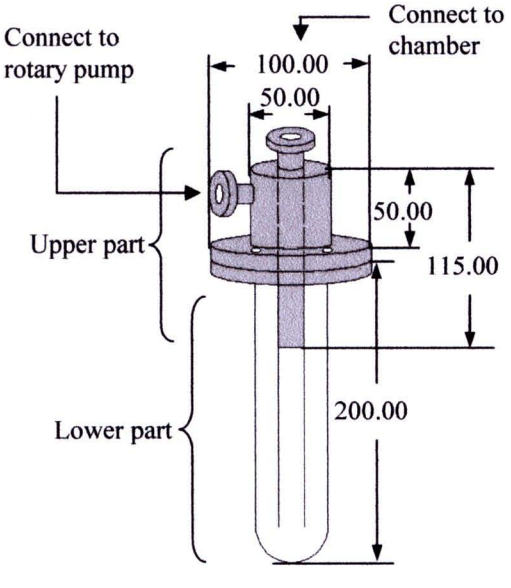
The cold trap was used as a link between the rotary vane pump and chamber. The cold trap was consisted of a glass tube (lower part) and was covered by stainless a steel plate (upper part). The upper part consisted of two ports. The top port was designed to connect a reactor chamber using NW 16 flange (**Appendix A.1**). The bottom part was designed to connect with an evacuation system (rotary pump). This compartment was designed to collect any residue monomer vapor which would pass

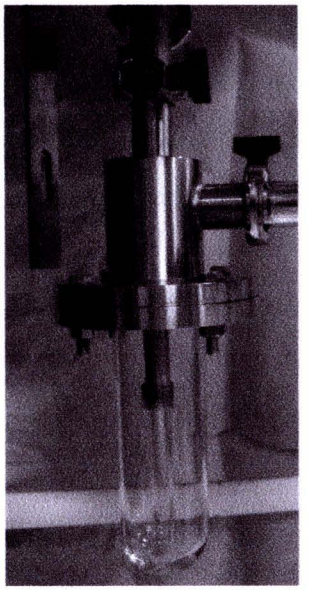
into the small inner tube and condense into a borosilicate receiver which uses dry ice and acetone as a coolant was covered the borosilicate receiver.



(a) AutoCAD Design (b) Monomer vessel

Figure 3.6 (a) The design of monomer vessel by AutoCAD program version 2007 in millimeter unit and (b) the photograph of the monomer vessel.





(a) AutoCAD Design (b) Cold trap

Figure 3.7 Illustration of the cold trap by AutoCAD program version 2007 (millimeter unit) (a) and the cold trap used in this study (b).

3.1.2 Testing of the AC system

Test runs had been performed to verify whether the system was ready to be utilized. Major concerns are as following:

3.1.2.1 Testing of the assembly under vacuum

The entire AC plasma reactor was assembled and tested for vacuum maintaining efficiency. The chamber was evacuated using a rotary pump until the chamber pressure approached to a relatively constant value. The base pressure was determined to be approximately 2×10^{-2} Torr. In general this base pressure can be reached within 60 minute. A relationship between the pressure (Torr) and a function of evacuation time (minute) was plotted as illustrated in **Figure 3.8**. After the base pressure had been achieved, the valve to the pump was closed and the assembly was tested for the ability to hold a vacuum. Again, a relationship between the pressure (Torr) and a function of time (minute) was plotted. The linear curve as shown in **Figure 3.9** showed an increase ratio of pressure with respective to time (approximately 0.0024 Torr/minute). It is indicated that air leakage into the chamber within 1 minute less than 0.3% when compared with pressure of 1 Torr. This proved that the system pressure was appropriate for the plasma technology which, in general, is in the pressure range of about 25 Torr to 1×10^{-5} Torr [60]. Attempts have been made to ensure that this can be reproduced when the reactor is in operation.

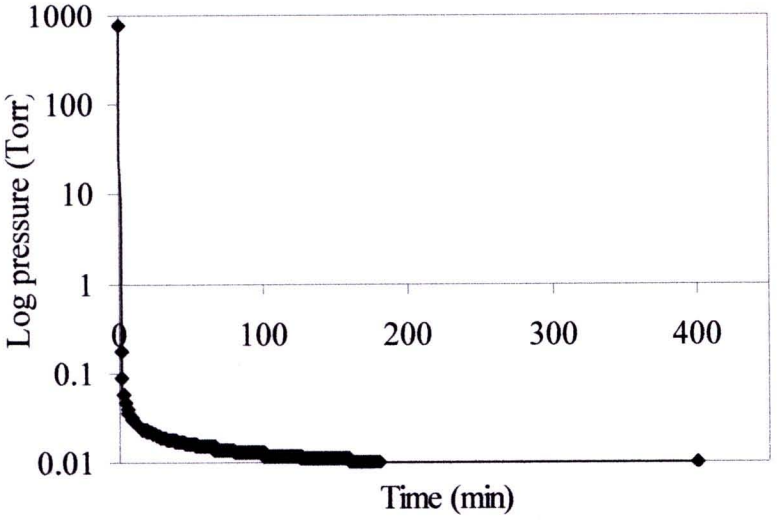


Figure 3.8 The graph of the decreasing pressure versus times.

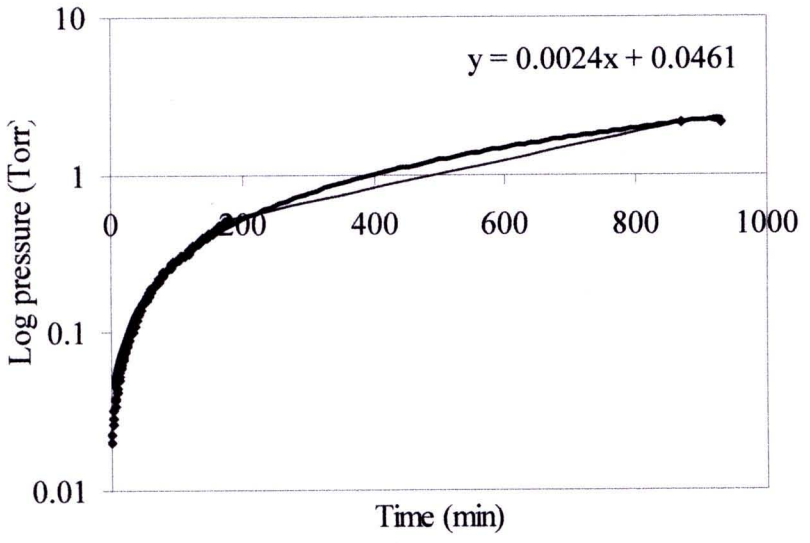


Figure 3.9 The graph of the increasing pressure versus times.

3.1.2.2 Testing of chemical recovery by cold trapping

The cold trap is a stainless steel which has a smaller internal stainless steel tube connected to the chamber. All excess vapor content from the reactor chamber was passed through the trap by means of a rotary pump. The trap was designed to let the residues pass through the inside tube (Region I) and condense with cooling. Then, the condensed liquid was collected in a borosilicate receiver (**Figure 3.10**). In order to check for trapping efficiency, pyrrole monomer was evaporated into the chamber without a AC transport and cooling system was applied.

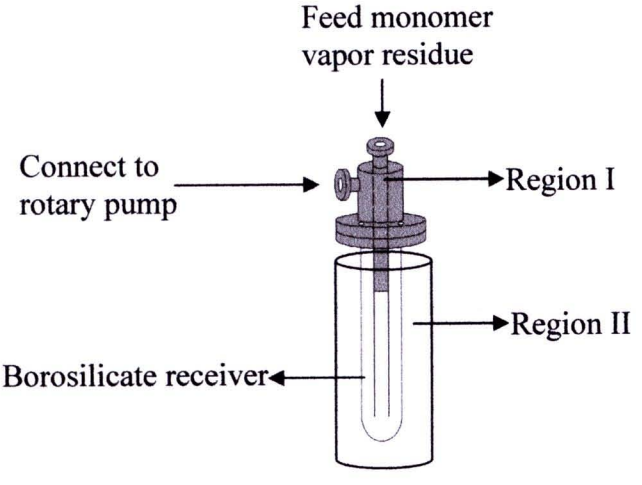


Figure 3.10 The cold trap showed region I for residues passing through the inside tube and region II for dry ice and acetone.

It was found that efficient trapping of all vapor content from the chamber outlet was achieved when adequate cooling with dry ice and acetone was applied in region II. Due to in pass of time had liquid pyrrole in a glass tube of cold trap.

3.1.2.3 Testing of power supply

The step up circuit consisted of a transformer, an ammeter, and a voltmeter. The transformer was used to increase voltage of AC power supply before transfer to the electrode of chamber. Also the ammeter and voltmeter were employed to detect current in circuit and voltage between electrodes during plasma generation, respectively. Prior to generation of plasma; the voltmeter and ammeter were calibrated with the multimeter (**Figures 3.11** and **3.12**). **Figure 3.11** shows voltage from transformer, power supply and multimeter. From **Figure 3.11**, the voltage of transformer was similar to that of multimeter; beside there was an increased approximately 10:1 compare with the voltage of AC power supply. The ammeter part was calibrated with multimeter, as shown in **Figure 3.12**. The current of circuit was 0.0001(x) + 0.0004 as show in **Table 3.1**.

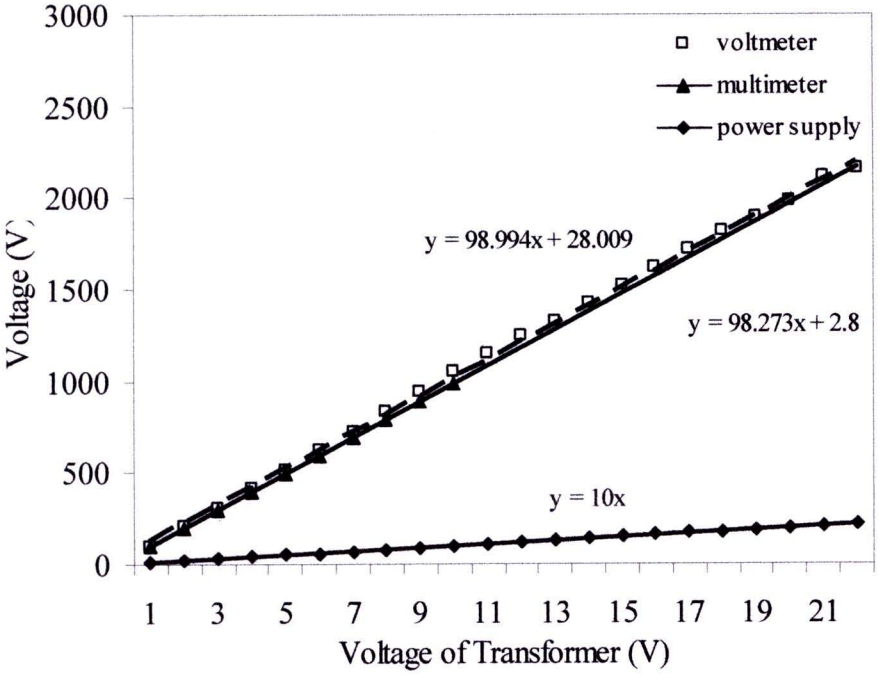


Figure 3.11 The linear graph showing the calibration of voltage for multimeter with voltmeter

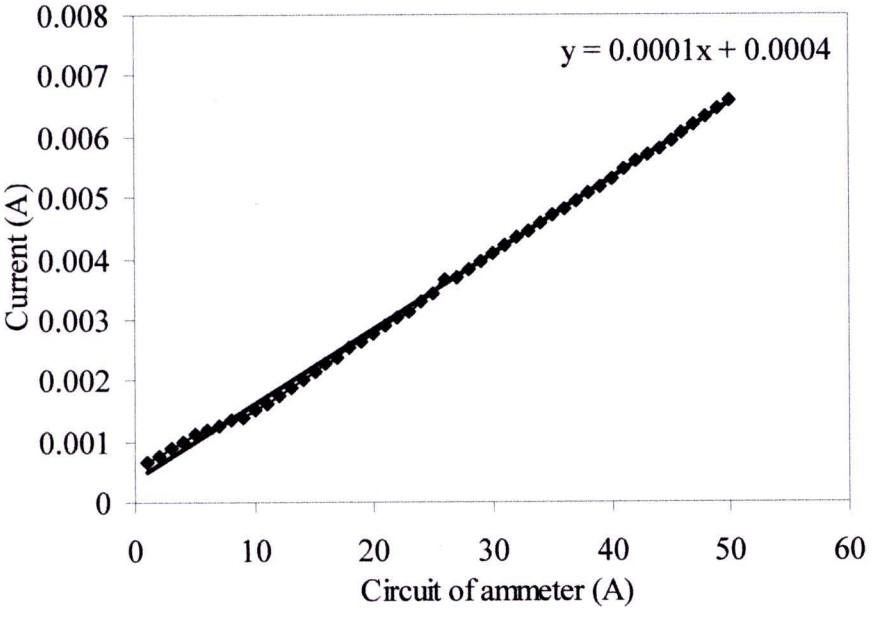


Figure 3.12 The linear graph showing the calibration of current for multimeter with ammeter

Table 3.1 The current of step up circuit.

Ammeter (mA)	current of circuit (A)
1	0.50
5	0.90
10	1.40
15	1.90
20	2.40
25	2.90
30	3.40
35	3.90
40	4.40
45	4.90
50	5.40

3.1.2.4 Determination of plasma temperature

The plasma diagnostics technique optical emission spectroscopy (OES) allows an identification of reactive species and gives information on the energetic properties of plasma. The main advantage of OES comparing to other plasma diagnostics techniques is its non-intrusive character [61].

In the measurement step, at the beginning, the chamber was evacuated with a rotary pump to the base pressure of around 0.02 Torr. Then a nitrogen flow was introduced into the chamber to provide the desired pressure. Subsequently, the input voltage was supplied to generate plasma glow discharge in the chamber. During the time of plasma glow the plasma illuminated in a violet pale pink color. Characterization of plasma phase was analyzed by OES. An HR4000 spectrophotometer including an OOIBase 32 software program was employed in the OES. Spectra were recorded from 300 to 1100 nm at 0.40 torr with an input AC voltage of 1000 V and a nitrogen flow rate of 5 sccm (mL/min). The measuring probe was placed at the outside of the chamber (**Figure 3.13**).

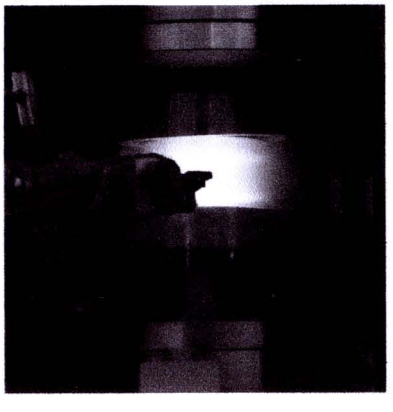


Figure 3.13 Position of OES probe during plasma temperature measurement

In the OES spectrum depicted in **Figure 3.14**, most of the N I peaks were observed in the range of 750-900 nm. The emission spectra data of nitrogen were obtained from NIST Atomic Spectra Database [62]. **Table 3.2** lists the spectroscopic data needed for the nine nitrogen transition used in this work. From the OES result, a graph between ratio of N II peak intensity to that of N I vs. electron temperature in accordance with Boltzmann equation (3.1) [20] was plotted. From the

intensity ratio of N II (at 746.98 nm) and N I (at 870.38 nm) it can be seen that both regions of the spectrum have a high transition probability. The electron temperature (T_e) can then be determined from the graph to be approximately 1.38 eV as shown in **Figure 3.15**.

$$R = \frac{I_2}{I_1} = (\frac{A_2}{A_1})(\frac{g_2}{g_1})(\frac{\lambda_1}{\lambda_2}) \cdot \exp(-(E_2 - E_1)/kT_e) \tag{3.1}$$

When R = Ratio

I = Intensity line i

A_i = Transition probability line i

g_i = Statistical weight line i

λ_i = wavelength line i

E_i = Energy level line i

k = Boltzmann constraint

T_e = Electron temperature

Table 3.2 Nitrogen spectroscopic data at 0.4 Torr for 1000 V.

Spectrum	Wavelength (nm)	A_i (s^{-1})	E_i (cm^{-1})	g_i
N III	399.04	1.19×10^{10}	396584.80	4
N III	500.92	4.89×10^{9}	402705.60	6
N II	584.13	2.06×10^{7}	186511.58	5
N II	645.19	6.07×10^{9}	155126.73	5
N II	746.98	3.85×10^{9}	149187.80	5
N II	**748.37**	$\mathbf{3.83 \times 10^{8}}$	**148940.17**	**5**
N III	773.21	2.13×10^{8}	396574.90	6
N I	**870.38**	$\mathbf{5.54 \times 10^{6}}$	**114 894.00**	**4**
N I	888.37	1.51×10^{7}	112565.47	4
N III	893.30	1.73×10^{8}	309849.80	8
N II	905.28	7.00×10^{7}	202714.12	3

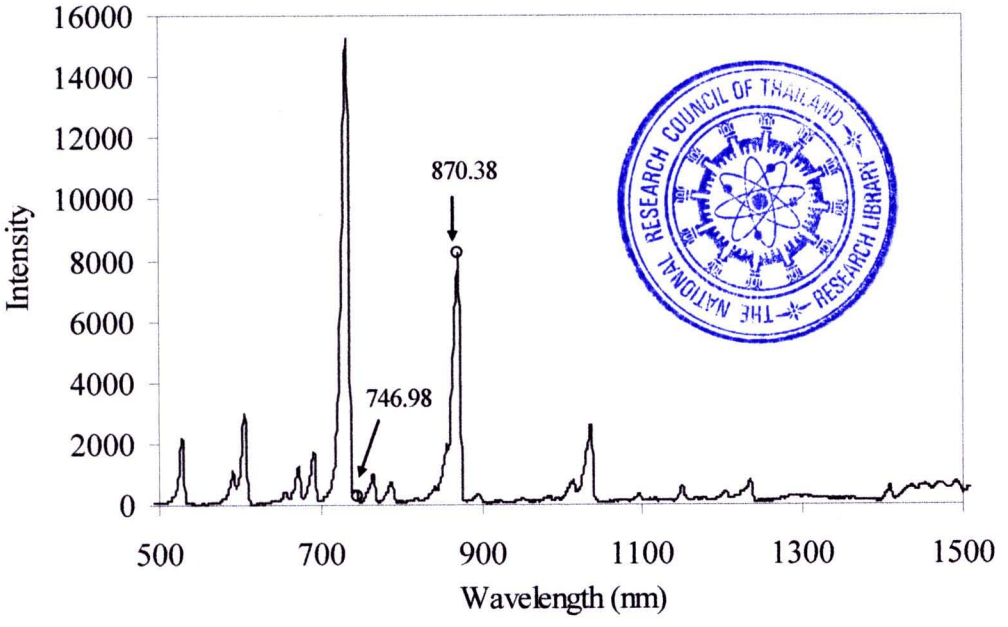


Figure 3.14 Optical emission spectrum of nitrogen plasma in the range of 500 to 1500 nm at 0.4 Torr for 1000 V.

Ratio = I_2/I_1 = 1395/547 = 2.55, T_e = 1.38 eV

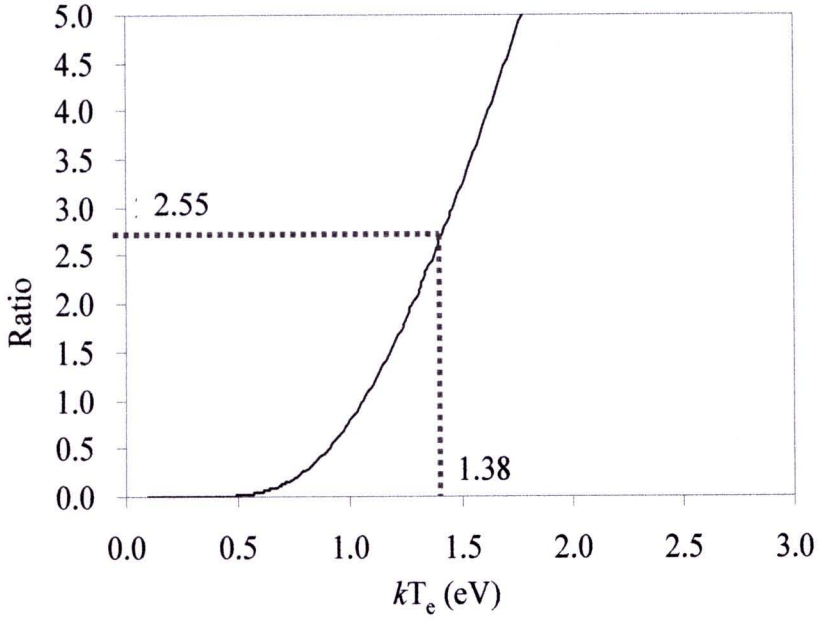


Figure 3.15 The peak intensity ratio versus electron temperature.

3.2 Experimental

3.2.1 Materials

All reagents and materials are analytical grade and used without further purification. Pyrrole was obtained from SIGMA-ALDRICH. Iodine, acetone, and methanol were purchased from MERCK. Nitrogen gas was purchased from TIG.

Fabricated polypyrrole films were analyzed with the following equipment. Characterization details are described in section **3.2.2**.

3.2.2 Equipment

The obtained films were subjected to thorough analyses by the following methods

3.2.2.1 Attenuated total reflection Fourier transform spectroscopy (ATR-FTIR)

ATR-FTIR investigates functional groups as well as structural relationships in films and the chemical states. The ATR spectra of polypyrrole films deposited on glass substrate were recorded using Continuum infrared microscope attached to the Nicolet 6700 FTIR spectrometer. The spectra were detected in the range of 750 - 4000 cm^{-1}. The plasma-polymerized polypyrrole was scraped from substrate and then ground with a mortar before characterization.

3.2.2.2 UV-visible absorption

UV-visible spectrophotometer model UV-2550 SHIMADZU was used to investigate surface absorption spectrum of polymer film in the range of 200-800 nm. Barium sulfate ($BaSO_4$) was used as a reference.

3.2.2.3 Scanning electron microscope

Surface morphology and film thickness were investigated using a JEOL, JSM-6480LV scanning electron microscope. A cross sectional mode was used

in the thickness measurement and each value reported herein was an average of five readings.

3.2.2.4 Energy-dispersive x-ray spectroscopy (EDS)

EDS is an analytical technique used for elemental analysis of samples. The technique utilizes x-rays that are emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. This study was performed on an OXFORD, INCAX-sight 7573. For quantitative analysis, samples were scanned at the 3000× magnification.

3.2.2.5 Electric conductivity

The electric conductivity was measured through the resistance measured using a two-probe. The current (I) was measured as a function of the applied voltage (V) from 0 to 100 V using HP 4140B *p*A meter / DC voltage source, including Lab View program.

3.2.3 Preparation of substrates

The previous of a plasma polymerization process, preparation of glass substrates need to be carried out. Glass substrates (1.5×2.5 cm^2) were first cleaned by acetone, methanol and deionized water in an ultrasonic bath for 5 minute, respectively. Subsequently, the clean substrates are dried in an oven at 100 °C for 5 minute then transferred to be kept in a desiccator completely for use. Substrates for preliminary experiments were carried out to determine optimum condition of the process.

Glass substrates which will be used in a fabrication process where electrical conductivity of the film would be measured are required to be treated by the following method prior to film fabrication. In order for the electrical conductivity of the film to be determined by a two-point probe measurement, these had two copper electrodes on each end of the glass substrates. This was conducted using a DC sputtering method operated at 0.004 Torr, 40 W, and 20 minute to afford coated copper electrodes with the size of 1.2×1.5 cm^2. After polypyrrole film deposition on the substrate, a sample would evidence as shown in **Figure 3.16**.

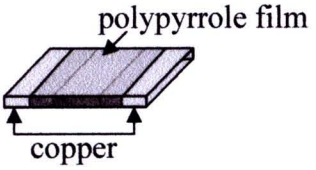


Figure 3.16 The substrate preparation for measurement of electrical conductivity.

3.2.4 Plasma polymerization of polypyrrole

At the beginning, the clean glass substrates were placed in the chamber (between electrodes), as shown in **Figure 3.17**. The system was first evacuated to the base pressure of around 0.02 torr. Then nitrogen gas was fed into the chamber to carry out plasma pre-treatment for 1 minute. In this pre-treatment step, the flow rate of nitrogen was fixed at 5 sccm, the pressure at 0.4 Torr and the AC voltage at 800 V. The same procedure was used for pre-treatment at 900, 1000, 1100, 1300, and 1500 V.

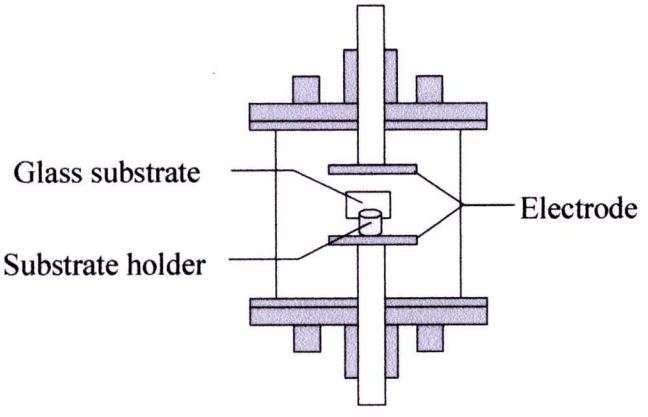


Figure 3.17 Schematic representation of the clean glass substrate in the chamber.

After the pre-treatment, nitrogen gas was bubbled through a reservoir of pyrrole in monomer vessel at room temperature. The monomer flowed into the chamber. The chamber was flooded with vapor of pyrrole and deposited on glass substrates during AC grow discharges. The condition of nitrogen gas flow rate and pressure of chamber were kept the same as conditions in the pre-treatment. The reaction time was kept at 30, 60, and 90 minutes. Voltages inputs of 800 , 900 , 1000 , 1100 , 1300 , and 1500 V were employed for igniting the glow discharge. After the

completion of plasma polymerization process, the films were exposed to air and kept in the desiccator for analyzed with various methods described in section **3.2.2**.

3.2.5 Plasma polymerization of polypyrrole and *in situ* doping with iodine

In doping method, iodine crystals were placed in a small glass tube and then placed into the chamber. The vacuum was applied to the system. As a consequence, iodine started to sublime more rapidly to generate a purple vapor all over the chamber. Subsequently pyrrole monomer purged with nitrogen gas was fed into the chamber. Then AC discharge was applied to generate plasma.

At the same time, OES technique was carried out to analyze the plasma phase to verify that iodine species were present. Sublimation of iodine was visible all over the chamber. When plasma-polymerization was taking place, OES analysis was performed to ensure the presence of iodine as well as to identify active iodine species involved in the experiments. OES spectrum taken at 1000 V was shown in **Figure 3.18**. Iodine peaks were observed in the OES spectrum at 607.57 nm, 719.55 nm, 722.90 nm, 873.53 nm, and 1095.22 nm as shown in **Figure 3.17** [62].

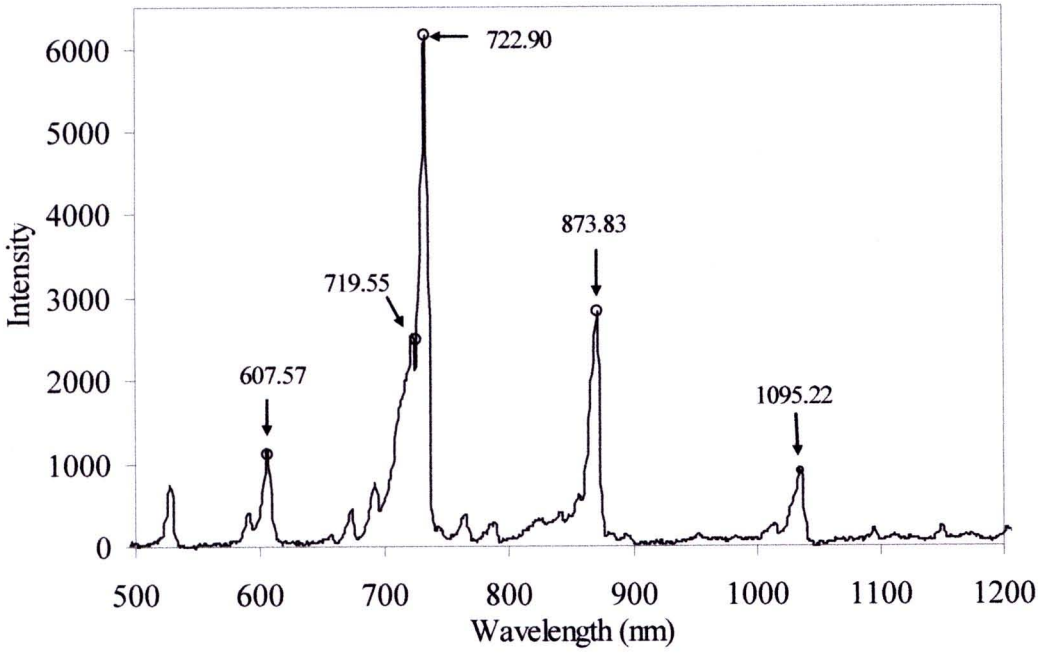


Figure 3.18 OES spectrum of iodine-doped plasma-polymerized polypyrrole.

The measuring probe was placed at the outside of the chamber at which the plasma discharge can be seen. The plasma polymerized films were produced at the AC voltages of 800 to 1500 V. The polymerization times were 30, 60 and 90 minutes; the chamber pressure during film growing was maintained at approximately 0.4 Torr. The *in situ* doping plasma-polymerized polypyrrole films were carried out in three series. The series of reaction times were 30, 60, and 90 minutes, respectively. For each reaction condition, for example at 800 V and 30 minute, experiments were carried out in triplicate. Therefore, eighteen samples were obtained in each series and a total of fifty-four samples were subsequently analyzed. Glass substrates fabricated with iodine doped polypyrrole were analyzed with various methods described in section **3.2.2**.

3.2.6 Chemical synthesis of polypyrrole

Liquid bromine (0.15 mL) was added to acetonitrile (250 mL). Pyrrole (0.7 mL) was slowly added to the bromine solution. The mixture vigorously stirred about 16 hours at room temperature. After the reaction, the solution was poured into an acetonitrile to obtain precipitate. The precipitate was rinsed thoroughly with copious amount of dichloromethane and methanol consecutively. The polymer was dry at ambient temperature to obtain a black polymer. It was wash thoroughly with dichloromethane, dried under vacuum at room temperature and kept in a desiccator.