CHAPTER V

CONCLUSION AND SUGGESTIONS

The home-made economical prototype AC plasma system was designed and constructed for polypyrrole synthesis. This system can be divided into two main parts; plasma part and chemical part. In the plasma part, it is consisted of a vacuum chamber, and power supply. The vacuum chamber was made from a glass cylinder with both ends covered by stainless steel plates. The voltage was transferred from the AC power supply to the transformer. At this point, the voltage of transformer was increased tenfold. This voltage was further transferred to the electrodes in the chamber. Another main part, the chemical part is comprised of monomer vessel, and cold trap. Liquid monomer was filled into monomer vessel Nitrogen gas was then added which carries monomer vapor into the chamber. The cold trap was connected between the chamber and the Edwards rotary vane pump to collect condensed residue monomer vapor, resulted from cool surrounding environment (dry ice and acetone). The optical emission spectroscopy (OES) technique was used to determine electron temperature (T_e) in plasma reactor. The results revealed that T_e of argon plasma was 1.38 eV at 0.4 torr, 1000 V and nitrogen flow rate was 5 sccm.

The condition of voltage (800, 900, 1000, 1100, 1300, and 1500 V) and plasma polymerization time (30, 60, and 90 minute) were varied for the syntheses of polypyrrole films. The effect of AC power supply was explained by the increase in electron density with increasing AC voltage input which results in an increase in the number of collisions between electrons and other plasma species. And using short of plasma polymerization time and voltage as though the deposition of the monomer vapor was very low Therefore, polymerization time and voltage for film fabrication needed to be at least 30 minute and 800 V. The effect of AC voltage and plasma polymerization time on chemical structure, morphology, elemental composition, and electrical conductivity are summarized. The transmittance ATR-FTIR spectra at 2938 cm^{-1} are absent which represent a C-H aliphatic stretching bonds and the band at 2200 cm^{-1} assigned to C≡N stretching and/or an –N=C=O stretching. This result clearly indicates that the pyrrole ring is destructed by plasma polymerization. However, the absorption of N-H bending of amine and/or a C=C aromatic stretching at 1633 cm^{-1}. This peak was sign of a conjugated system in the polypyrrole chain and confirms existence of cyclic structure. The elemental compositions of plasma-polymerized pyrrole films have C/N ratio in the range 4.0 to 5.8. The C/N of plasma-polymerized polypyrrole films were similar the C/N of chemical synthesis (4.7) which higher than ideal polypyrrole (4.0). This result can also verify the pyrrole structure was damaged during plasma polymerization. The effect of various voltages on conductivity has been tested and the result showed that if the voltage increases, the conductivity will decrease. The electrical conductivity is in a range of 67.2×10^{-8}- 3.4×10^{-8} S/cm. The solid-state UV-Vis spectra showed an absorption maximum around 326 to 370 nm. In addition, the surface morphology of polypyrrole is smooth at the voltage less than 1100 V but it is grain on the surface once the voltage is higher than 1100 V. Besides, polypyrrole films are dense and pinhole-free films, and the thickness is about 0.33 to 5.8 μm.

The *in situ* doping with iodine is a novel method to increase the electrical conductivity. Firstly, the iodine vapor, initially in the crystal form, and monomer vapor were added into the vacuum chamber. After that, the voltage was applied in order to generate AC plasma. Then, the iodine-doped polypyrrole film was deposited on a glass substrate. The results from ATR-FTIR and EDS experiments indicated that iodine exists on the polypyrrole films because of the appearance of $-CI-CH_2$ and/or -CH_2-I around 1400 cm^{-1} . Moreover, the atom ratio of I/N in *in situ* iodine-doped polypyrrole films was in the range of 0.3 to 3.2. The *in situ* iodine-doped polypyrrole synthesized by AC plasma polymerization had λ_{max} around 385 to 431 nm, more than the one without iodine doping. The increase of λ_{max} has suggested that this *in situ* doping method is successful at increasing the conductivity.

Moreover, the *in situ* and *ex situ* doping methods were compared to check how stable of the conductivity. The conductivity of the iodine-doped polypyrrole film, synthesized from *in situ* doping method, at 800 V at different reaction times (30, 60, and 90 minutes) was 8.4×10^{-7} to 16.6×10^{-7} S/cm which were lower than of plasma-polymerized polypyrrole films, doped with *ex situ* doping or conventional doping method (6.8×10^{-7} to 32.0×10^{-7} S/cm) at the same conditions. However, after 5 hours, the conductivity of the product from *ex situ* doping method was almost totally lost whereas the one from *in situ* method still have high conductivity. This result has revealed that the *in situ* doping method is more stable than the conventional doping method.

In the future, the process of AC plasma polymerization could be optimized by varying some parameters, such as pressure, frequency wave, flow rate of feed gas, and so on since these parameters might affect the elemental composition of material and fragmentation during deposition [19, 68, 69]. Also, the chemical structure of monomer with substituent could be a choice to minimize fragmentation. For instance, the pyrrole monomer structure with electron-donating substituent such as methyl or ethyl groups was used as a monomer to minimize fragmentation during plasma polymerization. In the doping step, the starting materials (dopant) and the method for doping could be also optimized in order to obtain the highest electrical conductivity. In an earlier study, the use of plasma treatment technique after the doping process (*ex situ*) was investigated and the results showed that this technique improve both the conductivity and stability of iodine doped films [70]. This suggests that in the future the plasma treatment technique could be performed to keep the films' conductivity as high and long as possible.

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