# CHAPTER III

# Experimental

## 3.1 Instruments and materials

### 3.1.1 Instruments

- Infrared Spectrophotometer ; Perkin Elmer 1430
- Fourier Transform Infrared spectophotometer; Perkin-Elmer model 1720
- Differential Thermal Analysis ; Shimadsu Thermal Analysis Instrument DT-30
- Scanning Electron Microscope ; model JSM-T20
- Elemental analyzer ; Perkin Elmer, model 240 analyzer,USA
- Multimeter
- Potentiometer
- Digital multimeter
- Saturated calomel electrode
- Platinum electrode
- Evacuable die
- Hydraulic pressure
- Vacuum pump
- Vernier caliber

### 3.1.2 Materials

| | |
|---|---|
| Pyrrole | FLUKA |
| Thiophene | FLUKA |
| 3-Methylthiophene | FLUKA |
| Methanol | MERCK |
| Chloroform | MERCK |
| Acetonitrile | BDS LIMITED |
| Acetone | MERCK |
| Ferric chloride anhydrous | MERCK |
| Potassium thiocyanate (KSCN) | |
| Sodium hydroxide | MERCK |
| Conc. sulfuric acid | MERCK |
| Nitrogen gas | |
| Oxygen gas | |
| Silicone oil | |

## 3.2 Procedure

### 3.2.1 Synthesis of Polypyrrole

#### 3.2.1.1 Typical Procedure for Polypyrrole Synthesis

Ferric chloride solution in methanol was added into 100 ml three-neck glass reactor equipped with mechanical stirrer, gas inlet tube for bubbling the oxygen-free nitrogen, calcium chloride tube and a septum. Oxygen free nitrogen gas must be passed through silica gel, pyrogallol and conc. sulfuric acid before flowing to the $FeCl_3$ solution at 0 $^{o}C$ for 1 hr. After that the polymerization was started by injecting vacuum-distilled pyrrole through septum by syringe to the solution with continuous stirring. A black powder formed almost instantaneously, and as the reaction progressed the color of the solution turned from rusty orange to green. The polymerization reaction was quenched by adding copious amount of solvent (methanol) in order to dilute $FeCl_3$ solution. Then polymer powder was filtered and washed with methanol until the filtrate was colorless and contained no Fe(III), as indicated by testing with KSCN. The polymer powder was then washed with acetone and vacuumn dried in the desiccator at room temperature .

### 3.2.1.2 Variation of Reaction Temperature

The polymerization was carried out in $FeCl_3$ solution with 3 different concentrations, i.e., 20 ml of 1.5 M, 2.5 M and 3.5 M. In each concentration, 1.00 ml of pyrrole and reaction time 20 min were kept constant. However, the reaction temperature was varried as detailed in Table 3.1 .

Table 3.1 Synthesis of polypyrrole with various reaction temperature

| Sample No. | Conc. $FeCl_3$ in MeOH (M) | Reaction temperature (+2°C) |
|---|---|---|
| $PP_1$ | 1.5 | 0 |
| $PP_2$ | | 10 |
| $PP_3$ | | 20 |
| $PP_4$ | | 35 |
| $PP_5$ | | 50 |
| $PP_6$ | 2.5 | 0 |
| $PP_7$ | | 10 |
| $PP_8$ | | 20 |
| $PP_9$ | | 35 |
| $PP_{10}$ | | 50 |

| Sample No. | Conc. $FeCl_3$ in MeOH (M) | Reaction temperature (+2°C) |
|---|---|---|
| $PP_{11}$ | 3.5 | 0 |
| $PP_{12}$ | | 10 |
| $PP_{13}$ | | 20 |
| $PP_{14}$ | | 35 |
| $PP_{15}$ | | 50 |

### 3.2.1.3 Various of Concentration of $FeCl_3$ Solution

The polymerization was carried out in 20 ml of $FeCl_3$ solution with various concentrations from 0.3 M to 3.5 M. In each reaction 1.00 ml of pyrrole, reaction temperature 0 °C and reaction time 20 min were kept constant. However, the concentration of $FeCl_3$ solution was varried as detailed in Table 3.2 .

Table 3.2 Synthesis of polypyrrole with various concentration of $FeCl_3$ solution

| Sample No. | Conc. $FeCl_3$ in MeOH (M) | Mole ratio $FeCl_3$:pyrrole |
|---|---|---|
| $PP_{16}$ | 0.3 | 0.44 : 1 |
| $PP_{17}$ | 0.6 | 0.88 : 1 |
| $PP_{18}$ | 1.0 | 1.43 : 1 |
| $PP_1$ | 1.5 | 2.14 : 1 |
| $PP_{19}$ | 2.0 | 2.86 : 1 |
| $PP_6$ | 2.5 | 3.57 : 1 |
| $PP_{20}$ | 3.0 | 4.29 : 1 |
| $PP_{11}$ | 3.5 | 5.55 : 1 |

### 3.2.1.4 Various Volume of $FeCl_3$ Solutions

The polymerization was carried out in 2.5 M $FeCl_3$ solution. In each reaction 1.00 ml of pyrrole, reaction temperature 0 $^{o}C$ and reaction time 20 min were kept constant. However the volume of $FeCl_3$ solution was varried as detailed in Table 3.3 .

Table 3.3 Synthesis of polypyrrole with various volume of solutions

| Sample No. | Volume of $FeCl_3$ solution (ml) | Mole ratio pyrrole : $FeCl_3$ |
|---|---|---|
| $PP_{21}$ | 15 | 1 : 2.68 |
| $PP_6$ | 20 | 1 : 3.57 |
| $PP_{22}$ | 30 | 1 : 5.36 |
| $PP_{23}$ | 40 | 1 : 7.14 |
| $PP_{24}$ | 50 | 1 : 8.93 |

### 3.2.1.5 Various Reaction Times

The polymerization was carried out in 20 ml of 2.5 M $FeCl_3$ solution . In each reaction 1.00 ml of pyrrole, reaction temperature 0 $^{o}C$ were kept constant. However the reaction time was varried as detailed in Table 3.4 .

Table 3.4 Synthesis of polypyrrole with various reaction times

| Sample No. | Reaction time (min) |
|---|---|
| $PP_{25}$ | 5 |
| $PP_{26}$ | 10 |
| $PP_6$ | 20 |
| $PP_{27}$ | 30 |
| $PP_{28}$ | 40 |
| $PP_{29}$ | 60 |

### 3.2.1.6 Various Solvents

The polymerization was carried out by varried ratios of mix-solvents (MeOH:$CHCl_3$). In each reaction 20 ml of 2.5 M $FeCl_3$ solution, 1.00 ml of pyrrole, reaction temperature 0 $^{o}C$ and reaction time 20 min were kept constant. The ratio of mix-solvent was varried as detailed in Table 3.5 .

Table 3.5 Synthesis of polypyrrole with various solvents

| Sample No. | Volume of solvent MeOH + $CHCl_3$ (ml) | Ratio MeOH : $CHCl_3$ |
|---|---|---|
| $PP_6$ | 20 + 0 | |
| $PP_{30}$ | 18 + 2 | 9 : 1 |
| $PP_{31}$ | 16 + 4 | 4 : 1 |
| $PP_{32}$ | 15 + 5 | 3 : 1 |
| $PP_{33}$ | 10 + 10 | 1 : 1 |
| $PP_{34}$ | 5 + 15 | 1 : 3 |
| $PP_{35}$ | 0 + 20 | |

### 3.2.2 Conductivity Measurement

Polymer powder was pressed into disc form ( ø = 1.20 cm.) by hydraulic pressure in special evacuable die. After that the conductivities of pressed disc polymers were measured by Van der Pauw method (see section 2.3)

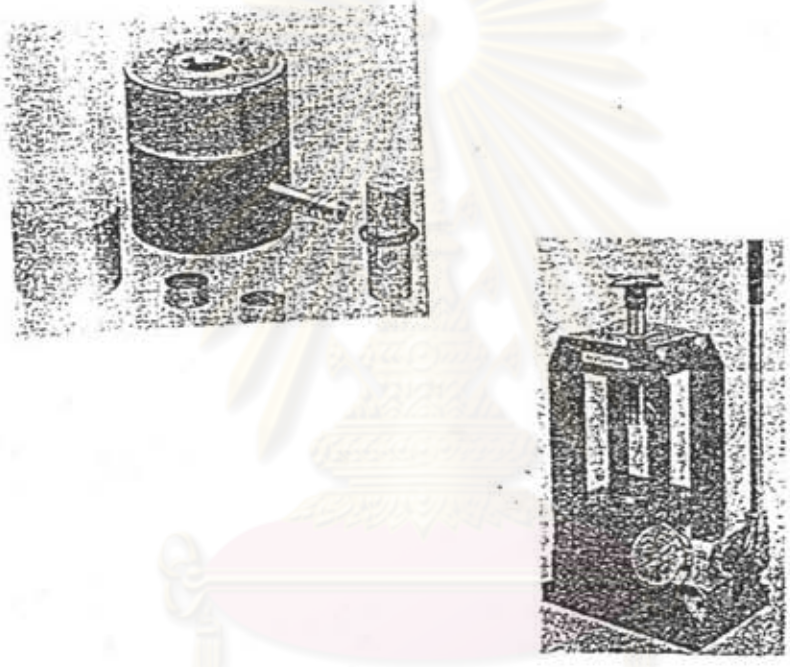

Figure 3.1 Evacuable die and hydraulic pressure

3.2.2.1 The Optimum Pressure for Pressed Polymer Disc

Firstly,the pressing force for pressing polypyrrole into disc was varied from 2-6 tons. The conductivity of each sample was measured as shows in Table 3.6.

Table 3.6 Effect of pressure pressed on polymer disc

| Sample No.* | Conductivity ($Scm^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Pressing force (ton) | | | | |
| | 2 | 3 | 4 | 5 | 6 |
| $PP_1$ | 57.11 | 57.03 | 56.02 | 40.13 | 31.16 |
| $PP_6$ | 133.02 | 130.35 | 131.21 | 92.25 | 86.36 |
| $PP_{11}$ | 72.44 | 69.26 | 68.31 | 53.18 | 47.24 |

* See experimental 3.2.1.2

It was chosen to use 2 tons of force for preparing the polymer disc throughout this work.

3.2.2.2 The Decay Conductivity of Disc Polymer

Two samples of polypyrrole disc, as obtained in section 3.2 , were separately kept in open air at room temperature for a period of time to investigate the decay of conductivities.

3.2.2.3 The Stability of the Conductivity of Polymer in Various Conditions

3.2.2.3.1 Temperature

Polypyrrole powder, as obtained in section 3.2, was kept in the sealed package at various temperatures from 4 $^{o}$C to 100 $^{o}$C for a certain period of time. The conductivity of each sample was measured.

3.2.2.3.2 Acid/Base Solution

Polypyrrole powder, as obtained in section 3.2 which was separately exposed to sulfuric acid solution and sodium hydroxide solution. The concentration of each solution was varied from 0.25 M to 1.00 M. The samples were kept in the solutions at room temperature for 7 days. Then they were washed with deionized water and let dry in the desiccator under reduced pressure. The conductivity of each sample was recorded.

3.2.2.3.3 Atmosphere

Three samples of polypyrrole powder, obtained in section 3.2 , were separately kept in the sealed package full of oxygen or nitrogen. The other samples was exposed to dry air in desiccator. All three samples were allowed to stand, as specified above, at room temperature for one month. Then the conductivity of each sample was recorded.

### 3.2.3 Synthesis of Polythiophene

#### 3.2.3.1 Synthesis of Polythiophene in Methanol

Synthesis of polythiophene by chemical polymerization in solution was carried out using the same procedure as mention in section 3.2.1.1 but thiophene was used instead of pyrrole. In each reaction 20 ml of $FeCl_3$ in methanol solution was kept constant as detailed in Table 3.7.

Table 3.7 Condition for synthesis of polythiophen in methanol solution

| Sample No. | Conc. $FeCl_3$ in MeOH (M) | Reaction temperature ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $PT_1$ | 0.5 | 0 | 20 |
| $PT_2$ | | room | 20 |
| $PT_3$ | | 50 | 20 |
| $PT_4$ | 1.0 | 0 | 20 |
| $PT_5$ | | room | 20 |
| $PT_6$ | | 50 | 20 |

| Sample No. | Conc. $FeCl_3$ in MeOH (M) | Reaction temperature ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $PT_7$ | 1.5 | 0 | 20 |
| $PT_8$ | | room | 20 |
| $PT_9$ | | 50 | 20 |
| $PT_{10}$ | 2.5 | 0 | 20 |
| $PT_{11}$ | | 0 | 30 |
| $PT_{12}$ | | 0 | 60 |
| $PT_{13}$ | | room | 20 |
| $PT_{14}$ | | 50 | 20 |
| $PT_{15}$ | 3.5 | 0 | 20 |
| $PT_{16}$ | | 0 | 30 |
| $PT_{17}$ | | 0 | 60 |
| $PT_{18}$ | | room | 20 |

3.2.3.2 Synthesis of Polythiophene in Chloroform

Synthesis of polythiophene by chemical polymerization in solution was carried out using the same procedure as mention insection 3.2.3.1 but chloroform was used instead of methanol.In each reaction 20 ml of $FeCl_3$ in chloroform solution was kept constant as detailed in Table 3.8.

Table 3.8 Conditions for synthesis of polythiophene in chloroform solution

| Sample NO. | Conc. $FeCl_3$ in $CHCl_3$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $PT_{19}$ | 0.5 | 0 | 20 |
| $PT_{20}$ | | room | 20 |
| $PT_{21}$ | 1.0 | 0 | 20 |
| $PT_{22}$ | | room | 20 |
| $PT_{23}$ | 1.2 | 0 | 20 |
| $PT_{24}$ | | 0 | 40 |
| $PT_{25}$ | | 0 | 60 |
| $PT_{26}$ | | room | 20 |
| $PT_{27}$ | 1.5 | 0 | 20 |
| $PT_{28}$ | | room | 20 |

| Sample NO. | Conc. $FeCl_3$ in $CHCl_3$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $PT_{29}$ | 2.5 | 0 | 20 |
| $PT_{30}$ | | room | 20 |
| $PT_{31}$ | 3.5 | 0 | 20 |
| $PT_{32}$ | | room | 20 |
| $PT_{33}$ | 4.0 | 0 | 20 |
| $PT_{34}$ | | room | 20 |

3.2.3.3 Synthesis of Polythiophene in Acetonitrile

Synthesis of polythiophene by chemical polymerization in solution was carried out using the same procedure as mentioned insection 3.2.3.2 but acetonitrile was used instead of chloroform. In each reaction 20 ml of $FeCl_3$ in acetonitrile solution was kept constant as detailed in Table 3.9.

Table 3.9 Condition for synthesis of polythiophen in acetonitrile solution

| Sample NO. | Conc. $FeCl_3$ in $CH_3CN$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $PT_{35}$ | 0.3 | 0 | 20 |
| $PT_{36}$ | | room | 20 |
| $PT_{37}$ | 0.6 | 0 | 20 |
| $PT_{38}$ | | room | 20 |
| $PT_{39}$ | 1.0 | 0 | 20 |
| $PT_{40}$ | | room | 20 |
| $PT_{41}$ | 2.5 | 0 | 20 |
| $PT_{42}$ | | room | 20 |
| $PT_{43}$ | 2.8 | 0 | 5 |
| $PT_{44}$ | | | 15 |
| $PT_{45}$ | | | 30 |
| $PT_{46}$ | | room | 5 |
| $PT_{47}$ | | | 15 |
| $PT_{48}$ | | | 30 |

| Sample NO. | Conc. $FeCl_3$ in $CH_3CN$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $PT_{49}$ | 3.5 | 0 | 20 |
| $PT_{50}$ | | room | 20 |
| $PT_{51}$ | 4.0 | 0 | 20 |
| $PT_{52}$ | | room | 20 |

### 3.2.4 Synthesis of Poly (3-methylthiophene)

#### 3.2.4.1 Synthesis of Poly (3-methylthiophene) in Methanol

Synthesis of poly(3-methylthiophene) by chemical polymerization in solution was carried out using the same procedure as mention in section 3.2.3.1 but 3-methylthiophene was used instead of thiophene. In each reaction 20 ml of $FeCl_3$ in methanol solution was kept constant as detailed in Table 3.10.

Table 3.10 Condition for synthesis of poly(3-methylthiophene) in methanol solution

| Sample No. | Conc. $FeCl_3$ in $CH_3OH$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $P3MT_1$ | 0.5 | 0 | 20 |
| $P3MT_2$ | | room | 20 |
| $P3MT_3$ | | 50 | 20 |
| $P3MT_4$ | 1.0 | 0 | 20 |
| $P3MT_5$ | | room | 20 |
| $P3MT_6$ | | 50 | 20 |

| Sample No. | Conc. $FeCl_3$ in $CH_3OH$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $P3MT_7$ | 1.5 | 0 | 20 |
| $P3MT_8$ | | room | 20 |
| $P3MT_9$ | | 50 | 20 |
| $P3MT_{10}$ | 2.5 | 0 | 20 |
| $P3MT_{11}$ | | 0 | 30 |
| $P3MT_{12}$ | | 0 | 60 |
| $P3MT_{13}$ | | room | 20 |
| $P3MT_{14}$ | | 50 | 20 |
| $P3MT_{15}$ | 3.5 | 0 | 20 |
| $P3MT_{16}$ | | 0 | 30 |
| $P3MT_{17}$ | | 0 | 60 |
| $P3MT_{18}$ | | room | 20 |

### 3.2.4.2 Synthesis of Poly (3-methylthiophene) in Chloroform

Synthesis of poly(3-methylthiophene) by chemical polymerization in solution was carried out using the same procedure as mentioned insection 3.2.4.1 but chloroform was used instead of methanol. In each reaction 20 ml of $FeCl_3$ in chloroform solution was kept constant as detailed in Table 3.11.

Table 3.11 Condition for synthesis of poly(3-methylthiophene) in chloroform solution

| Sample NO. | Conc. $FeCl_3$ in $CHCl_3$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $P3MT_{19}$ | 0.3 | 0 | 20 |
| $P3MT_{20}$ | | room | 20 |
| $P3MT_{21}$ | 0.6 | 0 | 20 |
| $P3MT_{22}$ | | | 30 |
| $P3MT_{23}$ | | room | 20 |

| Sample NO. | Conc. $FeCl_3$ in $CHCl_3$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $P3MT_{24}$ | 1.0 | 0 | 20 |
| $P3MT_{25}$ | | | 30 |
| $P3MT_{26}$ | | room | 20 |
| $P3MT_{27}$ | 1.2 | 0 | 20 |
| $P3MT_{28}$ | | room | 20 |

3.2.4.3 Synthesis of Poly (3-methylthiophene) in Acetonitrile

Synthesis of poly(3-methylthiophene) by chemical polymerization in solution was carried out using the same procedure as mentioned in section 3.2.4.2, but acetonitrile was used instead of chloroform. In each reaction 20 ml of $FeCl_3$ in acetonitrile solution was kept constant as detailed in Table 3.12.

Table 3.12 Condition for synthesis of poly(3-methylthiophene) in acetonitrile solution

| Sample NO. | Conc. $FeCl_3$ in $CH_3CN$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $P3MT_{29}$ | 0.3 | 0 | 20 |
| $P3MT_{30}$ | | room | 20 |
| $P3MT_{31}$ | 0.6 | 0 | 20 |
| $P3MT_{32}$ | | room | 20 |
| $P3MT_{33}$ | 1.0 | 0 | 20 |
| $P3MT_{34}$ | | room | 20 |
| $P3MT_{35}$ | 2.5 | 0 | 20 |
| $P3MT_{36}$ | | room | 20 |
| $P3MT_{37}$ | 2.8 | 0 | 5 |
| $P3MT_{38}$ | | | 15 |
| $P3MT_{39}$ | | | 30 |
| $P3MT_{40}$ | | room | 5 |
| $P3MT_{41}$ | | | 15 |
| $P3MT_{42}$ | | | 30 |

| Sample NO. | Conc. $FeCl_3$ in $CH_3CN$ (M) | Reaction temp. ($^oC$) | Reaction time (min) |
|---|---|---|---|
| $P3MT_{43}$ | 3.5 | 0 | 20 |
| $P3MT_{44}$ | | room | 20 |
| $P3MT_{45}$ | 4.0 | 0 | 20 |
| $P3MT_{46}$ | | room | 20 |