

CHAPTER II

EXPERIMENTAL SECTION

2.1 Chemicals

1. Thiophene	:	Fluka
2. 3-Hexylthiophene	:	Aldrich
3. Ferric chloride anhydrous	:	Riedel-deHaën
4. <i>m</i> -Chloroperoxybenzoic acid	:	Aldrich
5. 30% Hydrogen peroxide	:	Merck
6. Trifluoroacetic acid	:	Fluka
7. 65% Perchloric acid	:	Carlo Erba
8. 70% Nitric acid	:	Labscan
9. Methanesulfonic acid	:	Fluka
10. Potassium permanganate	:	Merck
11. Copper sulfate pentahydrate	:	Merck
12. Peroxymonosulfate triple salts (oxone)	:	Riedel-deHaën
13. Tetrabutylammonium sulphate	:	Fluka
14. Benzyltriethylammonium chloride	:	Fluka
15. <i>N</i> -Benzylcinchodinium chloride	:	Fluka
16. Methylmorpholine <i>N</i> -oxide	:	Aldrich
17. Urea hydrogen peroxide	:	Merck
18. Dimethylsulfoxide	:	Fluka
19. Trimethylamine <i>N</i> -oxide dihydrate	:	Fluka
20. Sulfuric acid	:	Labscan
21. Pyridine <i>N</i> -oxide	:	Fluka
22. Toluene-4-sulfonic acid (TsOH)	:	Merck
23. Oxone tetrabutylammonium salt	:	Fluka
24. Sodium hydroxide	:	Merck
25. Sodium bisulphite	:	Merck

26. Methanol	:	Labscan
27. Dichloromethane	:	BDH
28. Chloroform	:	BDH
29. Deuterated chloroform	:	Merck
30. Potassium bromide	:	Merck

2.2 Instrument and apparatus

1. Infrared Spectrophotometer : Perkin Elmer or Nicolet (Impact 410)
2. Nuclear Magnetic Resonance Spectrometer : Varian, ACF 400 MHz
3. UV-Visible Spectrophotometer : HP 8453
4. Four-point probe conductometer : assembled by Assoc.Prof. Anuvat Sirivat

2.3 Synthesis of polythiophene (PT)

PT has been synthesized using conditions and mole ratios of starting materials as shown in **Table 3.1**. The following is an example: To a stirred suspension of 1.94 g (12 mmol) of FeCl_3 in 27 mL of methylene chloride, 0.74 g (9 mmol) thiophene was added dropwise at 0 °C. After 6 h, the reaction mixture was allowed to warm to room temperature and stirred overnight. Methanol was added to the mixture resulting in the formation of brown precipitates. The precipitates were collected by filtration and subsequently extracted with methanol to remove FeCl_3 residue using a soxhlet apparatus for 15 h. PT was obtained as brown powder in varied yields according to Table 1. The product was insoluble in all organic solvents, therefore, characterization by conventional methods was not possible. IR (KBr): 3070, 2920, 2850, 1640, 1430, 790, 690 cm^{-1} .

2.4 Synthesis of poly(3-hexylthiophene)⁴⁰ (P3HT)

P3HT has been synthesized using many conditions and mole ratios of starting materials as shown in **Table 3.2**. The following is an example: To a stirred suspension of 0.377 g (1 mmol) FeCl_3 in 11 mL of dichloromethane was added dropwise 0.168 g (2.33 mmol) of 3-hexylthiophene. The mixture was stirred overnight at ambient temperature. It was then worked up with methanol and centrifuged to let

precipitate of P3HT settle. Repeated methanol wash and centrifuge until the solution was no longer yellow. Solvent was removed and extracted with methanol using a soxhlet apparatus for 5 h. The crude polymer was redissolved in chloroform, and insoluble products were filtered off. P3HT was obtained as a black solid in varied yields according to Table 2. The product was soluble in toluene, THF, and chloroform. $\lambda_{\max}(\text{CHCl}_3) = 436 \text{ nm}$ $^1\text{H-NMR} (\text{CDCl}_3)$: δ 6.97 (s, 1H), 2.8 (broad, 2H), 1.7-1.3 (broad m, 4H), 0.91 (broad m, 3H). IR (KBr): 2920, 2855, 1510, 1460, 1380, 1190, 1110, 1020, 825, 725, 670 cm^{-1} .

2.5 Oxidation of PT

2.5.1 One-pot method

To a stirred suspension of 1.94 g (12 mmol) FeCl_3 in 27 mL of dichloromethane was added dropwise 0.74 g (9 mmol) of thiophene and 0.746 g (3 mmol) *m*CPBA at 0°C. After 6 h, the reaction mixture was allowed to warm to room temperature and stirred overnight. Methanol was added to the mixture resulting in the formation of brown precipitates. The precipitates were collected by filtration and subsequently extracted with methanol to remove FeCl_3 residue using a soxhlet apparatus for 15 h. PT was obtained as brown powder in varied yields according to **Table 3.3**. The final product dissolved only sparingly in chloroform and dichloromethane.

2.5.2 Consecutive method

2.5.2.1 By 70% $\text{HNO}_3/\text{CH}_3\text{SO}_3\text{H}$ ⁴¹

In a 10 mL round bottom flask, 70% nitric acid (0.73 mL, 12 mmol) was added, and the reaction was cooled to 0 °C. Then, methanesulfonic acid (2 g, 21 mmol) was added and the mixture was stirred for 10 min. To this solution, PT (0.5 g, 6 mmol) was added in one portion which turned black immediately. The mixture was vigorously stirred at 0 °C for 3 h, then at room temperature for 3 days. Samples of reaction mixture were collected to follow the progress of the reaction at 10th minute. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol.

The experiment was repeated with increased reaction time to 30 min, 70 min, 2 h, 3 h, 4 h, 6 h, 1 day, 2 days and 3 days to monitor progress of reaction.

2.5.2.2 By *m*CPBA^{42, 43}

A suspension of PT (0.01 g, 0.12 mmol) in CH₂Cl₂ (2 mL) was cooled to 0 °C in an ice water bath, *m*CPBA (0.15 g, 0.6 mmol) was then added to this mixture and stirred for 15 min, after which the ice bath was removed and the solution was allowed to warm to room temperature. After 24 h, reaction was quenched by an addition of a large amount of methanol into the reaction flask. The solvent was removed by filtration and the residue was washed repeatedly with methanol. The reaction was repeated with acetone and acetonitrile instead of dichloromethane.

2.5.2.3 By H₂O₂⁴⁴

PT powder (0.01 g, 0.12 mmol) was suspended in CH₂Cl₂ (4 mL) and 30% H₂O₂ (3 mL, 26.4 mmol) was added to this mixture with vigorous stirring at room temperature for 24 h. The reaction was quenched by pouring into 20 mL 5% NaHSO₃. The reaction has been repeated with additional reaction time of 5 h, 8 h and 20 h.

2.5.2.4 By H₂O₂/AcOH⁴⁵

PT powder (0.01 g, 0.12 mmol) was suspended in AcOH (2 mL) and 30% H₂O₂ (3 mL, 26.4 mmol) was added to this mixture with vigorous stirring. The mixture was stirred at room temperature for 24 h. The reaction was quenched by adding methanol. The solvent was removed by filtration and the residue was washed repeatedly with methanol. The residue was dried in vacuum. The reaction was repeated with stirring at 0 °C for 2 h and then at room temperature for additional 22 h.

2.5.2.5 By *m*CPBA/ FeCl₃⁴⁶

PT powder (0.01 g, 0.12 mmol) and FeCl₃ (0.78 g, 4.8 mmol) were suspended in 14 mL acetone in an ice bath and *m*CPBA (0.60 g, 2.4 mmol) was added to this mixture and stirred for 15 min, after which the ice bath was removed. The solution was allowed to warm to room temperature with stirring for additional 24 h. The reaction was quenched by adding methanol. The solvent was filtered from the

reaction mixture, and the residue was dried. The reaction was repeated with acetonitrile.

2.5.2.6 By $\text{H}_2\text{O}_2/\text{TFA}$ ⁴⁷

PT powder (0.01 g, 0.12 mmol) was suspended in dichloromethane (2 mL) and 30% H_2O_2 (3 mL, 26.4 mmol) was added to this mixture and the reaction was cooled to 0 °C. TFA (0.37 mL, 4.8 mmol) was added and the mixture was stirred for 15 min and then the solution was allowed to warm to room temperature. After 24 h, reaction was quenched by pouring a large amount of methanol into the reaction flask. Solvent was removed by filtration and the residue was washed repeatedly with methanol.

2.6 Oxidation of P3HT

In all cases, the reaction was followed by UV-visible spectrophotometry.

2.6.1 By 70% $\text{HNO}_3/\text{CH}_3\text{SO}_3\text{H}$ ⁴¹

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), 70% nitric acid (0.3 mL, 5 mmol) was added, and the reaction was cooled to 0 °C. Then, methanesulfonic acid (0.8 g, 8.3 mmol) was added and the mixture was stirred for 10 min. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The reaction was repeated without any solvent.

2.6.2 By *m*CPBA^{42, 43}

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL) was cooled to 0 °C in an ice bath. To this mixture was added *m*CPBA (50 mg, 0.2 mmol) and stirred for 10 min, after which the ice bath was removed and the solution was allowed to warm to room temperature. After 30 min, reaction was quenched by pouring a large amount of methanol into the reaction flask. Solvent was removed by filtration and the residue was washed repeatedly with methanol.

The reaction was repeated with increased reaction time to 10 min, 20 min, 40 min, 50 min, 60 min, 90 min, 120 min, 150 min, 180 min and 210 min.

2.6.3 By H_2O_2 ⁴²⁻⁴⁴

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL) was added 30% aqueous H_2O_2 (1 g, 8.8 mmol) and the mixture was vigorously stirred at room temperature for 1 day. Reaction was quenched by pouring a large amount of methanol into the reaction flask. Solvent was removed by filtration and the residue was washed repeatedly with methanol. The reaction was repeated with reflux for 1 day.

2.6.4 By $\text{KMnO}_4/\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ⁴⁸

Equal weights of potassium permanganate and copper sulfate pentahydrate were ground together in a mortar. The resulting fine, highly colored product was then used as a heterogeneous oxidant in CH_2Cl_2 solutions. A solution of P3HT (3.36 mg, 0.02 mmol) in 2 mL of dichloromethane and the prepared oxidant (0.5 g, 1.6 mmol KMnO_4 and 1 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were placed in a 10 mL round-bottomed flask and stirred vigorously at room temperature. After 72 h, the product was filtered and the residue was washed successively with dichloromethane. Evaporation of the solvent gave the product. The reaction was repeated with chloroform and benzene.

2.6.5 By $\text{H}_2\text{O}_2/\text{CF}_3\text{COOH}$ ⁴⁷

P3HT (3.36 g, 0.02 mmol) was dissolved in chloroform (2 mL) and 30% H_2O_2 (0.68 g, 6 mmol) was added to this mixture and the reaction was cooled to 0 °C. TFA (0.13 mL, 0.8 mmol) was added and the mixture was stirred for 10 min. Then, reaction was quenched by extracting the mixture with 0.1M NaHSO_3 (10 mL \times 3 times), the organic layer was dried over MgSO_4 , and evaporated.

The experiment was repeated with increased reaction time to 20 min, 40 min, 50 min, 60 min, 90 min, 120 min, 150 min, 180 min and 210 min and varied TFA 10 and 40 equivalence.

2.6.6 By Urea Hydrogen Peroxide (UHP)/TFA⁴⁷

P3HT (3.36 mg, 0.02 mmol) was dissolved in 2 mL chloroform and UHP (18.8 mg, 0.2 mmol) was added to the solution, which was cooled to 0 °C. TFA (0.13 mL, 0.8 mmol) was then slowly added to the reaction mixture (the reaction is exothermic). After 30 min the reaction was allowed to warm to room temperature and stirred for 24

h. The reaction was followed by UV-visible spectrophotometry every 4 h for the duration of 3 days. The reaction was quenched with an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ and stirred for 15 min to destroy any residual peroxides before being poured into a 0.5 mol HCl solution and extracted with CHCl_3 . The organic extracts were washed with saturated NaHCO_3 , dried over MgSO_4 and evaporated. The reaction was repeated at room temperature.

2.6.7 By Trimethylamine *N*-oxide Dihydrate (MNO)

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), MNO (0.5 g, 4.5 mmol) was added, and the reaction was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The experiment was repeated with reflux for 1 day and stirred at room temperature for 3 days.

2.6.8 By Pyridine *N*-oxide

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), pyridine *N*-oxide (0.5 g, 5.2 mmol) was added, and the reaction was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The experiment was repeated with reflux for 1 day and stirred at room temperature for 3 days. Also, aqueous pyridine *N*-oxide was used instead of solid pyridine *N*-oxide.

2.6.9 By Aqueous Oxone/Tetrabutylammonium Sulphate

P3HT (3.36 mg, 0.02 mmol) and a phase transfer catalyst (0.02 g) were dissolved in CH_2Cl_2 (2 mL) at room temperature. The solution was cooled to -10°C and an aqueous solution of oxone (0.2 g in 0.5 mL of water) was added. The reaction was stirred vigorously and allowed to warm slowly to room temperature and continued stirring for 24 h. Then the excess oxone was deactivated by the addition of 10% sodium metabisulfite. The organic layer was separated and evaporated to dryness.

The experiment was repeated with reflux for 1 day and stirred at room temperature for 3 days and varied phase transfer to benzyltriethylammonium chloride and *N*-benzylcinchlodinium chloride.

2.6.10 By UHP

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), UHP (37.6 mg, 0.4 mmol) was added, and the reaction was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The experiment was repeated with reflux for 1 day and stirred at room temperature for 3 days. Also, aqueous UHP was used instead of UHP.

2.6.11 By Methylmorpholine *N*-oxide

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), methylmorpholine *N*-oxide (0.5 g) was added, and the reaction was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The experiment was repeated with reflux for 1 day and stirred at room temperature for 3 days. Also, aqueous methylmorpholine *N*-oxide was used instead of methylmorpholine *N*-oxide.

2.6.12 By Methylmorpholine *N*-oxide/*m*CPBA

P3HT (3.36 g, 0.02 mmol) was dissolved in chloroform (2 mL) and methylmorpholine *N*-oxide (0.68 g, 6 mmol) was added to this mixture and the reaction was cooled to 0 °C. Then, *m*CPBA (0.13 mL, 0.8 mmol) was added and the mixture was stirred for 10 min. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The experiment was repeated at room temperature for 1 day, 3 days, and 5 days.

2.6.13 By UHP/Tetrabutylammonium Sulphate

P3HT (3.36 mg, 0.02 mmol) and a phase transfer catalyst (0.02 g) were dissolved in CH₂Cl₂ (2 mL) at room temperature. The solution was cooled to 0°C and

an aqueous solution of UHP (0.2 g in 0.5 mL of water) was added. The reaction was stirred vigorously and allowed to warm slowly to room temperature and continued stirring for additional 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The experiment was repeated with reflux for 1 day and stirred at room temperature for 3 days and varied phase transfer to benzyltriethylammonium chloride.

2.6.14 By 30% H₂O₂/Toluene-4-sulfonic acid (TsOH)

P3HT (3.36 g, 0.02 mmol) was dissolved in chloroform (2 mL) and 30% H₂O₂ (0.68 g, 6 mmol) was added to this mixture and the reaction was cooled to 0 °C. Then, TsOH (38 mg, 0.2 mmol) was added and the mixture was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol.

2.6.15 By H₂O₂/TFA

P3HT (3.36 g, 0.02 mmol) was dissolved in chloroform (2 mL) and 30% H₂O₂ (0.68 g, 6 mmol) was added to this mixture and the reaction was cooled to 0 °C. Then, TFA (13 mL, 0.2 mmol) was added and the mixture was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol.

2.6.16 By Peroxymonosulfate (oxone: KHSO₅)

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), oxone (0.5 g) was added, and the reaction was stirred for 24 h. The mixture was filtered and the organic part was quenched by methanol. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol.

2.6.17 By Oxone Tetrabutylammonium Salt

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), oxone tetrabutylammonium salt (0.5 g) was added, and the reaction was stirred for 24 h. The

reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol.

2.6.18 By Dimethyldioxirane⁴⁹

Oxone (0.5 g) was stirred in acetone (2 mL) for 48 h, then the mixture was filtered and dimethyldioxirane solution in acetone was collected.

To the solution of P3HT (3.36 mg, 0.02 mmol) in chloroform (2 mL), dimethyldioxirane solution (0.15 mL) was added, and the reaction was stirred for 24 h. The reactant was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol.

2.7 Preparation of cast film by oxidizing P3HT with H₂O₂/TFA

With the reaction in section 2.6.15 at time 0, 30, 60, 90 min, 18 mL of the reaction mixture was washed with 0.1 M NaOH three times until the mixture was no longer doped, indicated by UV-visible spectrophotometry. The organic phase was separated and dried with anhydrous MgSO₄. The solvent was evaporated until approximately 1.5 mL remained. The film was cast from this concentrated liquid on a Petri dish of 5 cm diameter. The cast film was cut to a circular shape of 3 cm diameter. Store the sample in a desiccator for 24 h.

2.8 Polymer Doping

2.8.1 PT Doped with HClO₄

HClO₄-doped PT was prepared by stirring suspension of PT (1.0 g, 12.4 mmol) in water 62 mL and certain amount of HClO₄ at room temperature for 3 days. The amounts of 65% HClO₄ used for low, medium and high doped polythiophene are shown in **Table 2.1**. The HClO₄ doped PT particles were filtered, vacuum dried for 2 h and ground to fine powder.

Table 2.1 The amount of 65% HClO_4 used for polythiophene doping

Entry	65% HClO_4 Volume (mL)	Final Acid Concentration (M)	Mole ratio PT: acid
1	1.1	0.2	1:1
2	5.5	1.0	1:5
3	11	2.0	1:10

2.8.2 P3HT Film Doped by Iodine Vapor

The polymer films, which was cut into the needed dimension, were dried in a vacuum oven for 24 h. The dried films were weighed, marked for identification, and placed in the iodine chamber. After finished, keep each film separately in an enclosed container.

2.8.3 P3HT Solution Doped by TFA

P3HT (0.05 mg, 0.3 μmol) was dissolved in 2 mL chloroform, measured the UV spectrum, added 20 μL TFA (0.26 μmol), then measured UV spectrum again every 10 min interval until the UV spectrum did not change. The experiment was repeated with TFA dosage of 40 μL (0.52 μmol).

2.8.4 P3HT Solution Doped by HClO_4

P3HT (0.05 mg, 0.3 μmol) was dissolved in 2 mL THF, measured the UV spectrum, added 5 μL 65% HClO_4 (0.084 μmol), then measured UV spectrum again every 10 min interval until the UV spectrum did not change.