

CHAPTER II

EXPERIMENTAL SECTION

2.1 Chemicals

1.	thiophene	:	Fluka
2.	3-hexylthiophene	:	ACROS organics
3.	ferric chloride anhydrous	:	Riedel-deHaën
4.	acetyl chloride	:	ACROS organics
5.	aluminium chloride anhydrous	:	Riedel-deHaën
6.	sodium hydrogen carbonate	:	Merck
7.	octaonyl chloride	:	ACROS organics
8.	magnesium sulfate anhydrous	:	Riedel-deHaën
9.	sodium sulfate anhydrous	:	Riedel-deHaën
10.	<i>N</i> -bromosuccinimide	:	ACROS organics
11.	chloroform	:	Lab-scan
12.	deuterated chloroform	:	Wilmad
13.	deuterated dimethyl sulfoxide	:	Wilmad
14.	methyl iodide	:	Riedel-deHaën
15.	dimethyl sulfate	:	ACROS organics
16.	silver trifluoromethanesulfonate	:	ACROS organics
17.	silver perchlorate hydrate	:	ACROS organics
18.	1,2-dichloroethane	:	Lab-scan
19.	anthranilic acid	:	BDH
20.	trifluoroacetic acid	:	Fluka
21.	isopentyl nitrite	:	Fluka
22.	tetrahydrofuran	:	Lab-scan
23.	copper acetate	:	Aldrich
24.	diphenyliodonium chloride	:	Fluka
25.	diphenyliodonium trifluoromethanesulfonate	:	Fluka

26. chlorobenzene : M&B
27. aniline : BDH
28. diethyl ether : Merck
29. Dichloromethane, hexane, ethyl acetate, and methanol were distilled before use : Italmar

2.2 Instruments and apparatus

1. Infrared Spectrophotometer: Perkin Elmer and Nicolet, Impact410
2. Nuclear Magnetic Resonance Spectrometer: Model Mercury plus 400 operated at 399.84 MHz for ^1H and 100.54 MHz for ^{13}C nuclei
3. UV-Visible Spectrophotometer: HP 8453
4. UV-Visible Spectrophotometer: Shimadzu UV-2550
5. Four-point probe conductometer: self-assembled by Assoc. Prof. Dr. Anuvat Sirivat, Petroleum and petrochemical college
6. Gel Permeation Chromatograph: Waters 600E
7. Centrifuge: Centurion 1000 series

2.3 Synthesis of Polythiophene (PT) [8]

To a stirred suspension of 0.65 g (4 mmol) of anhydrous FeCl_3 in 10 mL dichloromethane was added dropwise 0.25 g (3 mmol) of thiophene at 0 °C. After 6 h, the reaction mixture was allowed to warm to room temperature and stirred overnight for 18 h. Methanol was added to the mixture resulting in the formation of brown precipitate. Filtration of the precipitate and washing with methanol gave a brown powder in 90% yield (0.22 g). PT was insoluble in all organic solvents. IR (KBr): 3065, 1430, 1040, 790, 695 cm^{-1} . (**Figure A-1**, Appendix A)

2.4 Synthesis of Poly(3-hexylthiophene) (P3HT)

To a stirred suspension of 0.38 g (1 mmol) of anhydrous FeCl_3 in 10 mL dichloromethane was added dropwise 0.17 g (2.3 mmol) of 3-hexylthiophene. The reaction mixture was stirred at room temperature for 24 h. Methanol was added to the mixture resulting in the formation of brown precipitate. The precipitate was collected

by filtration and subsequently extracted with methanol to remove FeCl₃ residue using a soxhlet apparatus for 15 h. P3HT was obtained as a brown powder in 74% yield. P3HT was soluble in chloroform, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, and chlorobenzene. ¹H-NMR (CDCl₃): δ (ppm) 6.97 (1H), 2.8 (2H), 1.7–1.3 (4H), 0.9 (3H) (**Figure A-3**, Appendix A); IR (KBr): 3065, 2925, 2855, 1510, 1460, 1370, 1185, 825, 726 cm⁻¹ (**Figure A-2**, Appendix A); UV: λ_{max} (CH₂Cl₂): 440 nm. (**Figure A-15**, Appendix A)

2.5 Bromination of thiophene and PT derivatives

2.5.1 Bromination of thiophene

To the solution of 1.00 g (12 mmol) thiophene in 15 mL CH₂Cl₂-acetic acid (1:1) was added 4.65 g (26 mmol) of *N*-bromosuccinimide (NBS). The solution was refluxed for 30 min. The reaction mixture was then poured into saturated NaHCO₃ solution. After the organic layer was washed with water several times and dried over anhydrous MgSO₄, deep red liquid was obtained in 1.10 g (60% yield). ¹H-NMR (CDCl₃): δ (ppm) 6.9 (2H); IR (KBr): 3095, 1730, 1565, 1520, 1415, 1200, 987, 945, 790 cm⁻¹.

2.5.2 Bromination of PT

To the suspension of 0.078 g (0.95 mmol) PT in 10 mL CH₂Cl₂-acetic acid (1:1) was added 0.45 g (2.5 mmol) of NBS. The suspension was refluxed for 1 h. The reaction mixture was then poured into saturated NaHCO₃ solution. After filtration and washing with water several times, dark brown powder was obtained in 0.13 g (90 % yield based on fully dibrominated PT). Brominated polythiophene powder was insoluble in all organic solvents. IR (KBr) 1710, 1400, 1210, 1045 cm⁻¹.

2.5.3 Bromination of P3HT

Bromination of P3HT has been carried out using many conditions as shown in **Table 3.3**. The following is an example: To the solution of 0.0152 g (0.091 mmol) poly(3-hexylthiophene) in 10 mL CH₂Cl₂-acetic acid (1:1) was added 0.0249 g (0.14 mmol) of NBS. The solution was refluxed for 1 h. The reaction mixture was then poured into saturated NaHCO₃ solution. The organic layer was washed with water several times and dried over anhydrous MgSO₄. Precipitation into methanol gave yellow solid which was soluble in chloroform, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, and chlorobenzene. ¹H-NMR (CDCl₃): δ 7.1, 2.9–2.6, 1.7–1.3, 0.9;

IR (KBr): 2925, 2855, 1510, 1460, 1370, 1185, 825, 726 cm^{-1} ; λ_{max} (CH_2Cl_2): 342 nm.

2.6 Acylation of thiophene and PT derivatives

2.6.1 Acetylation of thiophene

To a solution of 2.50 g (30 mmol) thiophene in 3.0 mL (42 mmol) acetyl chloride, also used as solvent, was added 0.65 g (5 mmol) of AlCl_3 . The reaction mixture was stirred at ambient temperature for 24 h. The black solution mixture was quenched by water, extracted by saturated NaHCO_3 solution, washed with water several times, and dried over MgSO_4 . The crude mixture was obtained as black solution that cannot be identified or purified.

2.6.2 Acetylation of PT

To a suspension of 0.15 g (1.8 mmol) polythiophene in excess amount (5 mL) of acetyl chloride, also used as solvent, was added 0.26 g (2 mmol) of anhydrous AlCl_3 . The reaction mixture was stirred at ambient temperature for 24 h. Water was added to stop the reaction. Filtration of the suspension and washing with water several times gave 0.19 g of dark brown powder (83% yield assuming 100% substitution) which was insoluble in all organic solvents. IR (KBr): 3065, 1653, 1430, 1040, 790, 695 cm^{-1} (**Figure A-18**, Appendix A)

2.6.3 Octanoylation of PT

The similar procedure as described in 2.5.2 was followed using 0.05 g (0.6 mmol) polythiophene, 5 mL of octanoyl chloride, and 0.08 g (0.6 mmol) of AlCl_3 . The reaction mixture was stirred with reflux temperature for 33 hour. The black solution mixture was quenched by water and dichloromethane was added. The organic layer was extracted by a saturated NaHCO_3 solution and washed with water several times. After drying over anhydrous MgSO_4 and removal of solvent, a brown solid which soluble in chloroform, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, and chlorobenzene was obtained. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 2.6, 2.4, 1.7, 1.6, 1.3, 0.9 (**Figure A-20**, Appendix A); IR (KBr): 2925, 2855, 1650, 1460, 1370, 1185, 825, 726 cm^{-1} (**Figure A-19**, Appendix A).

2.6.4 Acetylation of P3HT

To a solution of 0.0044 g (0.026 mmol) poly(3-hexylthiophene) in excess amount (5 mL) of acetyl chloride, also used as solvent, was added 0.0035 g (0.026

mmol) of anhydrous AlCl_3 . The reaction mixture was stirred at reflux temperature for 2 h. The black solution mixture was quenched by water and dichloromethane was added. After working up procedure as describe in **2.5.3**, a brown solid which soluble in chloroform, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, and chlorobenzene was obtained in 96 % yield (0.0051 g) assuming 80% substitution. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 6.97, 2.8, 1.7–1.3, 0.9; IR (KBr): 3065, 2925, 2855, 1510, 1460, 1370, 1185, 825, 726 cm^{-1} ; UV: λ_{max} (CH_2Cl_2): 438 nm. The reaction has also been carried out in various conditions according to **Table 3.4**.

2.7 Arylation of thiophene

2.7.1 By anthranilic acid

To a stirred solution of 0.46 g (3.4 mmol) anthranilic acid and a drop of trifluoroacetic acid using as catalyst in 6 mL of tetrahydrofuran was added dropwise 0.8 mL (6.0 mmol) of isopentyl nitrite at 0°C . After 1.5 hours, the diazonium carboxylate precipitate was filtered with cooled tetrahydrofuran until the filtrate was colorless. Cooled 1,2-Dichloroethane was then used to replace tetrahydrofuran and to not let the precipitate dried. The diazonium carboxylate precipitate was added to a stirred solution of 0.56 g (6.7 mmol) thiophene in 10 mL of 1,2-dichloroethane. The reaction mixture was stirred for 4 hours at room temperature. Solvent was remove by evaporation. NMR (CDCl_3): δ (ppm) 8.2–7.5, 7.7, 7.6

2.8 Arylation of 3-hexylthiophene

2.8.1 By diphenyliodoniumchloride (DPIC)

To a stirred suspension of 0.0046 g (0.025 mmol) copper acetate in 0.0068 g (0.04 mmol) 3-hexylthiophene was added 0.0079 g (0.025 mmol) of diphenyliodonium chloride. The reaction mixture was heated to 140°C under nitrogen atmosphere. After one hour the reaction mixture was allowed to room temperature and characterized by NMR spectroscopy. NMR (CDCl_3): δ (ppm) 7.2, 7.0, 2.6, 1.6, 1.3, 0.9

2.9 Arylation of P3HT

2.9.1 By anthranilic acid

Handwritten signature

To a stirred solution of 0.12 g (1.2 mmol) anthranilic acid and a drop of trifluoroacetic acid using as catalyst in 5 mL of tetrahydrofuran was added dropwise 0.3 mL (2.2 mmol) of isopentyl nitrite at 0 °C. After 1.5 hours, the diazonium carboxylate precipitate was filtered with cooled tetrahydrofuran until the filtrate was colorless. Cooled 1, 2-Dichloroethane was then used to replace tetrahydrofuran and to not let the precipitate dried. The diazonium carboxylate precipitate was added to a stirred solution of 0.05 g (0.3 mmol) poly(3-hexylthiophene) in 5 mL of 1,2-dichloroethane. The reaction mixture was stirred for 3 hours at room temperature. Solvent was removed by evaporation. NMR(CDCl₃): δ (ppm) 6.97, 2.8, 1.7–1.3, 0.9

2.9.2 By DPIC

To a stirred suspension of 0.0004 g (0.002 mmol) copper acetate and 0.032 g (0.2 mmol) poly(3-hexylthiophene) in 5 mL of chlorobenzene was added 0.061 g (0.2 mmol) of diphenyliodonium chloride. The reaction mixture was reflux under nitrogen atmosphere. After one hour the reaction mixture was allowed to room temperature and characterized with NMR spectroscopy. NMR (CDCl₃): δ (ppm) 6.97, 2.8, 1.7–1.3, 0.9

2.9.3 By DPIC in NMR tube using Cu(OAc)₂

To an NMR tube containing a suspension of 0.0011 g (6 μmol) copper acetate and 0.0019 g (6 μmol) of diphenyliodonium chloride was added 0.0010 g (6 μmol) (3-hexylthiophene) in CDCl₃. The progress of the reaction was monitored by NMR spectroscopy immediately and daily when left in the tube at room temperature for one week. No significant change in NMR spectra was observed.

2.9.4 By DPIC in NMR tube using AgOTf

To an NMR tube containing a suspension of 0.0016 g (6 μmol) silver triflate and 0.0019 g (6 μmol) of diphenyliodonium chloride was added 0.0010 g (6 μmol) (3-hexylthiophene) in CDCl₃. The progress of the reaction was monitored by NMR spectroscopy immediately and daily when left in the tube at room temperature for one week. No significant change in NMR spectra was observed.

2.9.5 By diphenyliodonium triflate (DPIT)

To a stirred suspension of 0.0004 g (0.002 mmol) copper acetate in 0.032 g (0.2 mmol) poly(3-hexylthiophene) in 5 mL of chlorobenzene was added 0.009 g (0.02 mmol) of diphenyliodonium trifluoromethanesulfonate. The reaction mixture was reflux under nitrogen atmosphere. After one hour the reaction mixture was

allowed to room temperature and precipitated into ether. The precipitate could not dissolve in any solvent.

2.10 Methylation of thiophene

2.10.1 By methyl iodide (MeI)

To a stirred solution of 0.05 g (0.6 mmol) thiophene and 0.02 g (0.1 mmol) silver perchlorate hydrate in 5 mL of 1,2-dichloroethane was added 0.04 mL (0.6 mmol) methyl iodide at 0 °C. After 2 h, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The mixture was rinsed with 1,2-dichloroethane several times then purged with N₂ until dry. DMSO-d₆ was added to the mixture to dissolve the soluble product. NMR (DMSO-d₆) δ (ppm) 7.56, 7.15, 3.16.

2.11 Methylation of P3HT

2.11.1 By MeI

To a stirred suspension of 5 mg (60 μmol) poly(3-hexylthiophene) and 2 mg (10 μmol) silver perchlorate hydrate in 5 mL of 1,2-dichloroethane was added 0.02 mL (3 mmol) methyl iodide at 0 °C. After 2 h, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The mixture was poured into ether and centrifuged to collect the precipitate. This precipitate was insoluble in all organic solvents.

2.11.2 By MeI in NMR tube

To an NMR tube containing 1 mg (6 μmol) P3HT in CDCl₃ was added 0.02 mL (3 mmol) methyl iodide and small amount of silver trifluoromethanesulfonate (approximately 0.5 mg). The progress of the reaction was monitored by NMR spectroscopy immediately and daily when left in the tube at room temperature for one week. No significant change in NMR spectra was observed.

2.11.3 By dimethyl sulfate in NMR tube

To an NMR tube containing 1 mg (6 μmol) P3HT in CDCl₃ was added 0.02 mL (3 mmol) dimethylsulfate and small amount of silver trifluoromethanesulfonate (approximately 0.5 mg). The progress of the reaction was monitored by NMR spectroscopy immediately and daily when left in the tube at room temperature for one week. No significant change in NMR spectra was observed.