

CHAPTER II

EXPERIMENTAL SECTION

2.1 Chemicals

1. 3-hexylthiophene	:	Aldrich
2. thiophene	:	Merck
3. ferric chloride anhydrous	:	Riedel-deHaën
4. 30% hydrogen peroxide	:	Merck
5. trifluoroacetic acid	:	Lab-scan
6. hydrochloric acid	:	Merck
7. methanesulfonic acid	:	Fluka
8. toluene-4-sulfonic acid monohydrate	:	Fluka
9. iodine	:	Aldrich
10. urea hydrogen peroxide	:	Merck
11. sodium hydroxide	:	Merck
12. methanol	:	Lab-scan
13. dichloromethane	:	BDH
14. chloroform	:	BDH
15. acetone	:	Merck
16. deuterated chloroform	:	Merck
17. chloroacetic acid	:	ACROS organics
18. dichloroacetic acid	:	Fluka
19. trichloroacetic acid	:	CARLO ERBA
20. acetic acid	:	BDH
21. pyridine	:	Fluka
22. acetonitrile	:	Merck
23. hexane	:	Merck
24. triethylamine	:	ACROS organics
25. isobutylamine	:	Fluka

2.2 Instruments and apparatus

1. Infrared Spectrophotometer : Perkin Elmer and Nicolet, Impact 410
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 : Varian, CARY 100 Bio
5. Four-point probe conductometer : self-assembled by Assoc. Prof. Dr. Anuvat Sirivat
6. Gel Permeation Chromatograph : Water 600E
7. Matrix Assisted Laser Desorption/Ionization - Time Of Flight Mass Spectrometer : Bruker Daltonics, Omnixflex
8. Sonicator : Transsonic 570/H Elma
9. Centrifuge : MSE, Centaur 2, SANYO
10. Isotemp vacuum oven : Model 285 A Fisher Scientific
11. Conductometer : KEM CM-115 KYOTO ELECTRONICS

2.3 Synthesis of poly(3-hexylthiophene) (P3HT) [8,47]

3-Hexylthiophene 0.1683 g (1 mmol) was dissolved in 3 mL of dichloromethane and slowly added dropwise into a suspension of 0.3762 g (2.33 mmol) anhydrous FeCl_3 in 7 mL dichloromethane. When the addition was complete the mixture was stirred for 24 hr at room temperature. The polymer was precipitated by pouring the reaction mixture into 10% HCl in methanol. The precipitate was centrifuged and rinsed with a copious amount of methanol until the solution was no longer yellow. The remaining FeCl_3 was removed by Soxhlet extraction with methanol for 6 hr. The resulting polymer was then dried *in vacuo* to give a black solid in 82% yield (0.1380 g, 0.82 mmol). The product was soluble in toluene, THF, and chloroform. λ_{max} (CHCl_3) = 441 nm, $^1\text{H-NMR}$ (CDCl_3): δ 6.9-7.0 (1H), 2.5-2.8 (2H), 1.5-1.8 (2H), 1.2-1.5 (6H), 0.91 (3H) ppm. IR (KBr): 3050, 2953, 2921, 2852, 1513, 1458, 1369, 820, 723 cm^{-1} .

2.4 The fractionation of P3HT [45,46]

The polymer (0.2131 g) was first extracted after being dispersed in acetone 0.0288 g and stirred for 15 min. The suspension was filtered and washed with copious amount of acetone until the filtrate was colorless. The extractions of the precipitate were repeated, respectively with, hexane, CH_2Cl_2 , 10% CHCl_3 in CH_2Cl_2 , and CHCl_3 . Each separated filtrate was then evaporated to give fractions of P3HT, which was characterized by GPC, ^1H NMR and UV-visible spectroscopy (0.0017 g of each polymer fraction in 2 mL chloroform).

2.5 The doping of P3HT

2.5.1 Doping with trifluoroacetic acid (TFA)

P3HT (0.0017 g, 10 μmol) was dissolved in 2 mL chloroform. 60 μL of this solution was dissolved in 2 mL chloroform. 60 μL of this solution was added into 2 mL chloroform in a UV cell. UV-visible absorption of this solution was measured. Trifluoroacetic acid (TFA) was added incrementally according to **Table 2.1** and then measured its UV-visible absorption again every 5 min interval until no change in the absorption spectra was observed. The experiment was repeated with acetonitrile as the solvent.

Table 2.1 Equivalents of TFA

μL	mmol	$10^3 \times \text{equivalent}$
19	0.25	0.83
38	0.50	1.67
57	0.75	2.50
76	1.00	3.33
9.6	1.25	4.17
115	1.50	5.00
153	2.00	6.67
230	3.00	10.00

P3HT 0.3 μmol

2.5.2 Doping with methanesulfonic acid (MSA)

The same procedure as described in 2.5.1 was followed using concentration ratios of polymer to acid at 0.3 μmol : 0.1 mmol (0.33×10^3 equivalent) and 0.3 μmol : 0.15 mmol (0.50×10^3 equivalent).

2.5.3 Doping with acetic acid

The same procedure as described in 2.5.1 was followed using concentration ratios of polymer to acid ($\mu\text{mol}/\text{mmol}$) between 0.3/3 (10×10^3 equivalent) to 0.3/9 (30×10^3 equivalent) and didn't repeated with acetonitrile as the solvent.

2.5.4 Doping with chloroacetic acid (CA)

The same procedure as described in 2.5.3 was followed using concentration ratios of polymer to acid ($\mu\text{mol}/\text{mmol}$) between 0.3/1 (0.33×10^3 equivalent) to 0.3/3 (10×10^3 equivalent).

2.5.5 Doping with dichloroacetic acid (DCA)

The same procedure as described in 2.5.3 was followed using concentration ratios of polymer to acid ($\mu\text{mol}/\text{mmol}$) between 0.3/0.5 (1.67×10^3 equivalent) to 0.3/3 (10×10^3 equivalent).

2.5.6 Doping with trichloroacetic acid (TCA)

The same procedure as described in 2.5.3 was followed using concentration ratios of polymer to acid ($\mu\text{mol}/\text{mmol}$) between 0.3/0.5 (1.67×10^3 equivalent) to 0.3/3 (10×10^3 equivalent).

2.5.7 Doped with toluene-4-sulfonic acid monohydrate (TsOH.H₂O) and toluene-4-sulfonic acid (TsOH)

P3HT (0.0017 g, 10 μmol) was dissolved in 2 mL chloroform. 60 μL of this solution was dissolved in 2 mL chloroform. 60 μL of this solution was added into 2 mL chloroform in a UV cell. UV-visible absorption of this solution was measured. The acid was added into concentration ratios of polymer to acid 3 μmol : 0.25 mmol and then measured its UV-visible absorption again every 5 min interval until no change in the absorption spectra was observed.

TsOH H₂O was heated at 80 °C until its weight did not change. Then the same procedure was followed as the case of Toluene-4-sulfonic acid monohydrate (TsOH.H₂O).

2.6 The doping of P3HT fractions with TFA

Each fraction of P3HT from section 2.4 (0.0017 g, 10 μmol) was used in place of P3HT and the similar procedure as 2.5.1 was followed.

2.7 Oxidation of P3HT

2.7.1 By H₂O₂/TFA

P3HT (0.0250 g, 0.15 mmol) was dissolved in chloroform (12.5 mL) and measured the UV-visible spectrum. The reaction was cooled to 0 °C and 30% H₂O₂ (4.25 g, 37.5 mmol) was added to this mixture followed by TFA (0.28 mL, 3.72 mmol). At every 10 min, a 2 mL aliquot of the mixture was withdrawn from the reaction and was quenched with 0.1 M NaOH and monitored its UV-visible absorption until the UV-visible spectrum of the withdrawn sample did not show any significant changes.

2.7.2 By Urea Hydrogen Peroxide (UHP)/TFA

The same procedure as described in 2.7.1 was followed except this experiment used the UHP (3.52 g, 37.5 mmol). The experiment was repeated in which UHP and TFA were mixed first into a homogeneous solution in varied ratios according to Table 2.2 before adding into the P3HT solution. In entry 6 (Table 2.2), the reaction in the same manner was carried out but was heated to 50 °C

Table 2.2 Mole ratios of P3HT : UHP : TFA

entry	P3HT (mmol)	UHP (mmol)	TFA (mmol)	ratio P3HT : UHP : TFA
1	0.15	37.50	37.5	1 : 250 : 250
2	0.03	0.75	7.5	1 : 25 : 250
3	0.09	2.25	67.5	1 : 25 : 750
4	0.09	4.50	9.0	1 : 50 : 100
5	0.09	2.25	4.5	1 : 25 : 50
6 ^a	0.05	0.10	0.2	1 : 2 : 4

^aThe reaction was heated to 50 °C

2.8 Solvato-controlled doping

P3HT (0.0084 g, 0.05 mmol) was dissolved in chloroform and the solution was measured the UV- visible spectrum. Various pairs of acids (TsOH, MSA, DCA) and bases (H₂O, pyridine, triethylamine, thiophene, butylamine) were mixed according to Table 2.3, and added to the P3HT solution. Thin layer of this solution was spreaded onto the inner surface of one of the transparent windows of a UV cell. The cell was heated at 60 °C and monitored the UV-visible spectrum every 10 min interval until the UV-visible spectrum did not show any significant change.

Table 2.3 Mole ratios of P3HT : Acid : Base in solvato-controlled doping condition

Entry	Acid	Base	mmol			Mole ratios P3HT : Acid : Base
			P3HT	Acid	Base	
1	TSA	H ₂ O	1.5	1.5	1.5	1 : 1 : 1
2	MSA	pyridine	0.05	0.05	0.1	1 : 1 : 2
3	MSA	triethylamine	0.05	0.05	0.1	1 : 1 : 2
4	DCA	triethylamine	0.05	0.05	0.1	1 : 1 : 2
5	DCA	thiophene	0.05	0.1	0.2	1 : 2 : 4
6	DCA	thiophene	0.05	0.025	0.025	1 : 0.5 : 0.5
7	MSA	thiophene	0.1	0.05	0.1	1 : 0.5 : 1
8	MSA	triethylamine	0.1	0.05	0.1	1 : 0.5 : 1

2.9 Conductivity measurement

2.9.1 Polymer solution by conductometer

As synthesized P3HT or a fraction of P3HT from section 2.4 (0.0017 g, 10 μ mol) was dissolved in 1 mL of chloroform. This solution (270 μ L) was further diluted into 6 mL of chloroform. The temperature of the resulting solution was measured. Trifluoroacetic acid (TFA) was added at various mole ratios of polymer to acid as shown in **Table 2.4**. The conductivity of the mixture was measured after 5 min and compared to the conductivity of the control solution containing no P3HT.

Table 2.4 Equivalents of TFA for conductometric method

mL	M	mmol	$10^3 \times$ equivalent
0.17	0.36	2.25	0.83
0.34	0.71	4.50	1.67
0.51	1.04	6.75	2.50
0.68	1.35	9.00	3.33
0.85	1.64	11.25	4.17
1.02	1.92	13.50	5.00
1.36	2.44	18.00	6.67
2.04	3.36	27.00	10.00

P3HT 2.7 μ mol (0.45 mM)

2.9.2 Polymer film by 4-point probe

2.9.2.1 P3HT film doped by iodine vapor

A polymer film was cast by pouring a P3HT solution into a petri dish then heated to 40 ° to evaporate CHCl_3 . Thickness of four pieces of labeled polymer film, were measured and placed in an iodine chamber. After 24 hr, the four doped film pieces were left in an empty closed container for 4, 5, 6 and 7 hr, respectively. The conductivity of each film was measured immediately after being taken out of the container by a 4-point probe conductometer (Appendix B).

2.9.2.2 TCA-doped P3HT film

P3HT (0.0202 g, 120 μ mol) was dissolved in 1 mL chloroform. Trichloroacetic acid (TCA) was added at various ratios was shown in **Table 2.5** and films were cast as described in **2.9.2.1**, then the conductivity was measured (Appendix B).

Table 2.5 Equivalents of TFA for 4-point probe method

μmol	equivalent
30	0.25
60	0.50
120	1.00
240	2.00

P3HT 120 μmol