

## CHAPTER II

### EXPERIMENTAL SECTION

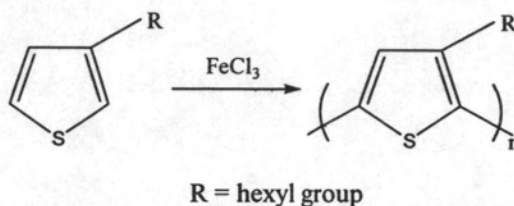
#### 2.1 Chemicals

1. acetone	:	Merck
2. aluminium chloride anhydrous	:	Riedel-deHaën
3. chloroform	:	Distilled from commercial grade
4. concentrated nitric acid	:	Lab-scan
5. concentrated sulfuric acid	:	Lab-scan
6. cyclohexane	:	Lab-scan
7. deuterated chloroform	:	Wilmad
8. dichloroethane	:	Lab-scan
9. dichloromethane	:	Distilled from commercial grade
10. dimethylformamide	:	Lab-scan
11. ferric chloride anhydrous	:	Riedel-deHaën
12. hexane	:	Distilled from commercial grade
13. 3-hexylthiophene	:	Aldrich
14. methanesulfonic acid	:	Fluka
15. methanol	:	Lab-scan
16. pyridine	:	Fluka
17. pyrrole	:	Acros organic
18. silver trifluoromethanesulfonate	:	Acros organic
19. thiophene	:	Merck
20. trichloroacetic acid	:	CARLO ERBA
21. trifluoroacetic acid	:	Lab-scan
22. titanium tetrachloride	:	Wilmad
23. zinc chloride	:	Fluka

## 2.2 Instruments and apparatus

1. Nuclear Magnetic Resonance Spectrometer : Mercury plus 400 operated at 399.84 MHz for  $^1\text{H}$  and 100.54 MHz for  $^{13}\text{C}$  nuclei
2. UV-visible Spectrophotometer : HP 8453 and UV-2550 SHIMADZU
3. Gel Permeation Chromatograph : Water 600E
4. Isotemp vacuum oven : Fisher Scientific 285 A

## 2.3 Synthesis of poly(3-hexylthiophene)



### 2.3.1 Effect of the mole ratios of 3-hexylthiophene to FeCl<sub>3</sub>

3-Hexylthiophene (0.1683 g, 1 mmol) was dissolved in dichloromethane 3 mL and slowly added dropwise into a suspension of anhydrous ferric chloride (0.2703 g, 1.66 mmol; mole ratio of 3-hexylthiophene : FeCl<sub>3</sub> = 1:1.66) in dichloromethane 6 mL. When the addition was completed, the mixture was stirred for additional 24 h at room temperature. The polymer was then precipitated by an addition of 20 mL of methanol. The precipitate was filtered and rinsed with methanol until the washed solution was colorless. The remaining ferric chloride in the precipitate was exhaustively removed by soxhlet extraction with methanol for 24 h. The resulting polymer was then dried to give black solid powder which was soluble in toluene, tetrahydrofuran, dichloromethane and chloroform. The reaction was repeated by varying the mole ratios of 3-hexylthiophene to FeCl<sub>3</sub> according to **Table 2.1**. The polymer was characterized by gel permeation chromatograph, <sup>1</sup>H NMR and UV-visible spectroscopy.

**Table 2.1** Weight of 3-hexylthiophene and FeCl<sub>3</sub> in various mole ratios

Mole ratio of 3-hexylthiophene : FeCl <sub>3</sub>	weight of 3-hexylthiophene (g)	weight of FeCl <sub>3</sub> (g)
1 : 1.66	0.1683	0.2703
1 : 2.33	0.1683	0.3785
1 : 3.00	0.1683	0.4866
1 : 3.66	0.1683	0.5947

## **2.3.2 Effect of reaction temperature**

### **2.3.2.1 At -22 °C**

P3HT was synthesized using the general procedure as in section 2.3.1 and the mole ratios of 3-hexylthiophene to anhydrous  $\text{FeCl}_3$  equals 1:3 with modification as follows: A suspension of  $\text{FeCl}_3$  (0.2703 g 1.66 mmol) in 6 mL  $\text{CH}_2\text{Cl}_2$  was cooled to 0 °C in an ice bath. 3-hexylthiophene (0.1683 g, 1 mmol) in 3 mL  $\text{CH}_2\text{Cl}_2$  was slowly added dropwise into this mixture and stirred for about 20 min. The mixture was then kept at -22 °C in a freezer for additional 24 h. The resulting polymer was quenched and washed following the rest of the procedure as in section 2.3.1.

### **2.3.2.2 At -50 °C**

The procedure in section 2.3.1 was repeated except that the reaction was cooled down and kept at approximately -40 to -50 °C in a dry ice bath.

### **2.3.2.3 At 61 °C**

The procedure in section 2.3.1 was repeated except that  $\text{CHCl}_3$  was used instead of  $\text{CH}_2\text{Cl}_2$  and the reaction was heated and kept at reflux temperature of the solvent in a sand bath.

## **2.3.3 Effect of the initial concentration of 3-hexylthiophene**

Four samples of 3-hexylthiophene 0.1683 g (1 mmol) were each dissolved in 1.5, 3, 6 and 9 mL of  $\text{CH}_2\text{Cl}_2$  respectively. Each solution was slowly added dropwise into a suspension of anhydrous  $\text{FeCl}_3$  0.4866 g (3 mmol) in  $\text{CH}_2\text{Cl}_2$  6 mL. When all the additions were completed, the reactions were stirred for additional 24 h at room temperature. The completed reactions were then washed following the same procedure as in section 2.3.1.

#### **2.3.4 Effect of the solvent**

The procedure in section 2.3.1 with the mole ratio of 3-hexylthiophene to ferric chloride equals 1:3 was repeated using other solvent including dichloroethane, toluene, chloroform and cyclohexane.

#### **2.3.5 Effect of the additives**

The procedure in section 2.3.1 with the mole ratio of 3-hexylthiophene to ferric chloride equals 1:3 was repeated with 12.1  $\mu\text{L}$  of  $\text{H}_2\text{O}$  (2.5%) was added prior to the addition of 3-hexylthiophene solution. Four more repetitions of the whole procedure were carried out with the different amount and type of additives as follow: 24.3  $\mu\text{L}$  of  $\text{H}_2\text{O}$  (5%), 48.6  $\mu\text{L}$  of  $\text{H}_2\text{O}$  (10 %), 27.5  $\mu\text{L}$  of conc.  $\text{H}_2\text{SO}_4$  (10%) and 32.6  $\mu\text{L}$  of trifluoroacetic acid (TFA) (10%).

### **2.4 Fractionation of P3HT**

#### **2.4.1 P3HT obtained from general procedure (section 2.3.1, mole ratios of 3-hexylthiophene to anhydrous $\text{FeCl}_3$ equals 3:9)**

P3HT from section 2.3.1 0.3 g was suspended by stirred in acetone for 30 min. The mixture was filtered and washed repeatedly with fresh acetone until the filtrate was colorless. The extraction procedure was repeated with the washed precipitate 3 more times with other solvents in the respective order : hexane, dichloromethane and chloroform. The collected filtrate from each fraction was then evaporated to give a solvent-specific soluble fraction of P3HT, which was characterized by UV-visible spectroscopy and gel permeation chromatograph.

#### **2.4.2 P3HT obtained from reaction with water added (section 2.3.5)**

The dark powder of 0.3 g of P3HT from section 2.3.5 which added water 2.5, 5 and 10% as synthesise was repeated the fractionation procedure as 2.4.1.

### 2.4.3 Digestion of the undissolved P3HT fraction

0.0133 g of the undissolved fraction of P3HT from section 2.4.2 (10% H<sub>2</sub>O) was added with concentrated nitric acid 2 mL and stirred for 1 h. The mixture was filtered and adjusted the volume to 5 mL with water in a volumetric flask and 250  $\mu$ L of this solution was again adjusted with water to 5 mL in another volumetric flask. This latter solution was measured the UV-visible absorption. 0.0133 g of undissolved fractions of P3HT from the other two samples (2.5 and 5% H<sub>2</sub>O) were repeated with the same procedure.

## 2.5 The doping of P3HT

### 2.5.1 Doping with protonic acids

Six samples of P3HT 0.0202 g (120  $\mu$ mol) dissolved in 1 mL CHCl<sub>3</sub> were each added TCA 0.0049 g (30  $\mu$ mol), 0.0098 g (60  $\mu$ mol), 0.0196 g (120  $\mu$ mol), 0.0391 g (240  $\mu$ mol), 0.0490 g (300  $\mu$ mol), 0.0588 g (360  $\mu$ mol) and TFA 9.1  $\mu$ L (120  $\mu$ mol), respectively. Each solution was dispersed onto a glass slide and heated in an oven at 60 °C for 30 min. The resulting thin film was measured by UV-visible spectrophotometer.

### 2.5.2 Doping with Lewis acids

Four samples of P3HT 0.0150 g (0.09 mmol) dissolved in 1 mL CHCl<sub>3</sub> were each added 0.18 mmol of AlCl<sub>3</sub> (0.024 g), FeCl<sub>3</sub> (0.029 g), ZnCl<sub>2</sub> (0.024 g) and TiCl<sub>4</sub> (~0.034 g). The mixture was stirred for 1 h and filtered. The resulting solution was measured the UV-visible absorption.

### 2.5.3 Doping of P3HT film

P3HT powder 0.015 g (0.09 mmol) was dissolved in 2 mL CHCl<sub>3</sub> and heated in an oven at 60 °C for 30 min, rinsed with methanol and heated in an oven at 60 °C for 30 min. The resulting dried film was dipped in liquid MSA for 20, 40, 60 min and measured by UV-visible spectrophotometer.

## 2.6 Solvato-controlled doping

P3HT (0.0170 g, 0.1 mmol) was dissolved in chloroform and the solution was measured by the UV-visible spectrophotometer. Various pairs of MSA and bases, (thiophene, pyrrole, pyridine, dimethylformamide and triethylamine) which were mixed according to **Table 2.2**, Lewis acids and ligands according to **Table 2.3**, were added to the P3HT solution. Thin layer of this solution was spreaded onto a glass slide and heated in an oven at 80 °C for 30 min. The resulting dried film was measured the UV-visible absorption.

**Table 2.2** Mole ratios of P3HT:MSA:base in solvato-controlled doping condition

Entry	Acid	Base	Amount used (mmol)			Mole ratios of P3HT:MSA:base
			P3HT	MSA	Base	
1	MSA	thiophene	0.1	0.025	0.2	1:0.25:2
2	MSA	thiophene	0.1	0.5	0.2	1:0.5:2
3	MSA	thiophene	0.1	0.1	0.2	1:1:2
4	MSA	thiophene	0.1	0.15	0.2	1:1.5:2
5	MSA	thiophene	0.1	0.2	0.2	1:2:2
6	MSA	pyridine	0.1	0.05	0.2	1:0.5:2
7	MSA	pyrrole	0.1	0.05	0.2	1:0.5:2
8	MSA	DMF	0.1	0.05	0.2	1:0.5:2

**Table 2.3** Mole ratios of P3HT:Lewis acid:ligand in solvato-controlled doping condition

Entry	Acid	Ligand	Amount used (mmol)			Mole ratios of P3HT:Lewis acid :ligand
			P3HT	Lewis acid	Ligand	
1	AlCl <sub>3</sub>	thiophene	0.1	0.05	0.2	1:0.5:2
2	AlCl <sub>3</sub>	pyridine	0.1	0.05	0.2	1:0.5:2
3	AlCl <sub>3</sub>	DMF	0.1	0.05	0.2	1:0.5:2
4	AlCl <sub>3</sub>	pyridine	0.1	0.1	0.2	1:1:2
5	AlCl <sub>3</sub>	TEA	0.1	0.1	0.2	1:1:2
6	AlCl <sub>3</sub>	pyridine	0.1	0.1	0.4	1:1:4
7	AlCl <sub>3</sub>	pyridine	0.1	0.2	0.4	1:2:4
8	FeCl <sub>3</sub>	thiophene	0.1	0.05	0.2	1:0.5:2
9	FeCl <sub>3</sub>	pyridine	0.1	0.05	0.2	1:0.5:2
10	FeCl <sub>3</sub>	DMF	0.1	0.05	0.2	1:0.5:2
11	FeCl <sub>3</sub>	pyridine	0.1	0.1	0.2	1:1:2
12	FeCl <sub>3</sub>	TEA	0.1	0.1	0.2	1:1:2
13	FeCl <sub>3</sub>	pyridine	0.1	0.1	0.4	1:1:4
14	FeCl <sub>3</sub>	pyridine	0.1	0.2	0.4	1:2:4
15	ZnCl <sub>2</sub>	pyridine	0.1	0.05	0.2	1:0.5:2
16	ZnCl <sub>2</sub>	pyridine	0.1	0.2	0.4	1:2:4
17	TiCl <sub>4</sub>	pyridine	0.1	0.05	0.2	1:0.5:2



## 2.7 Synthesis of Copolymer

3-hexylthiophene (0.0421 g, 0.25 mmol) and EDOT (0.0166 g, 0.75 mmol) were dissolved in dichloromethane 6 mL and slowly added dropwise into a suspension of anhydrous ferric chloride (0.4866 g, 9 mmol; mol ratio of 3-hexylthiophene : EDOT : FeCl<sub>3</sub> was 0.25:0.75:3) when the addition was completed, the mixture was stirred for additional 24 h at room temperature. The polymer was then precipitated by an addition of 20 mL of methanol. The precipitate was filtered and rinsed with methanol until the washed solution was colorless. The remaining ferric chloride in the precipitate was exhaustively removed by soxhlet extraction with methanol for 24 h. The resulting polymer was then dried to give black solid powder. The reaction was repeated by varying the mole ratios of 3-hexylthiophene, EDOT and FeCl<sub>3</sub> according to **Table 2.4**. The polymer was characterized by gel permeation chromatograph, <sup>1</sup>H NMR and UV-visible spectroscopy.

**Table 2.4** Weight of 3-hexylthiophene, EDOT and FeCl<sub>3</sub> in various mole ratios

Mole ratio			Weight (g)		
3-hexylthiophene	EDOT	FeCl <sub>3</sub>	3-hexylthiophene	EDOT	FeCl <sub>3</sub>
0.25	0.75	3	0.0421	0.1066	0.4866
0.5	0.5	3	0.0841	0.0710	0.4866
0.75	0.25	3	0.1262	0.0355	0.4866