REFERENCES

1. Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, $(CH)_x$. *J. Chem. Soc., Chem. Commun.* **1977**: 578-580.

2. (a) Tepveera, K. Synthesis and Electronic Properties of Polythiophene Containing Thienyl *S,S*-Dioxide Units. Master's Thesis, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, **2003**.

   (b) Bannarukkul, W. Effects of doping agents on optical and conductive properties of poly(3-hexylthiophene). Master's Thesis, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, **2005**.

3. Mullekom, H.A.M. The Chemistry of High and Low Band Gap Conjugated Polymers. Eindhoven University of Technology, the Netherlands, **2000**.

4. Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. Preparation of Soluble Polythiophene Derivative Utilizing Transition Metal Halides as Catalysts and Their Property. *Chemistry Express* **1986**: *1*, 635-638.

5. Chen, T –A.; Wu, X.; Rieke, R. D. Regiocontrolled Synthesis of Poly (3-alkylthiophenes) Mediated by Rieke Zinc: Their Characterization and Solid-State Properties. *J. Am. Chem. Soc.* **1995**: *117*, 233-244.

6. Nalwa, H. S., ed. Handbook of Organic Conductive Molecules and Polymers: Vol. 2. Spectroscopy and Physical Properties. *John Wiley & Sons* : Chichester, **1997**.

7. Tourillon, G.; Garnier, F. New Electrochemically Generated Organic Conducting Polymers. *J. Electroanal. Chem.* **1982**: *135*, 173-178.

8. Amou, S.; Haba, O.; Shirato, K.; Hayakawa, T.; Ueda, M.; Takeuchi, K.; Asai, M. Head-to-Tail Regioregularity of Poly(3-hexylthiophene) in Oxidative Coupling Polymerization with $FeCl_3$. *J. Polym. Sci. A: Polym. Chem.* **1999**: *37*, 1943-1948.

9. Niemi, V. M.; Knuuttila, P.; Österholm, J. -E.; Korvola, J. Polymerization of 3-alkylthiophenes with $FeCl_3$. *Polymer* **1992**: *33*, 1559-1562.

10. Allinger, N. L.; Walter T. J. Alkyl Group Isomerization in the Cross-Coupling Reaction of Secondary Alkyl Grignard Reagents with Organic Halides in the Presence of Nickel-Phosphine Complexes as Catalysts. *J. Am. Chem. Soc.* **1972**: *94*, 9268-9269.

11. Negishi, E. –I.; Takahashi T.; Baba, S.; Horn, D. E. V.; Okukado, N. Palladium- or Nickel-Catalyzed Reactions of Alkenylmetals with Unsaturated Organic Halides as a Selective Route to Arylated Alkenes and Conjugated Dienes: Scope, Limitations, and Mechanism. *J. Am. Chem. Soc.* **1987**: *109*, 2393-2401.

12.Chen, T.–A.; Rieke, R. D. The First Regioregular Head-to-Tail Poly(3-hexylthiophene-2,5-diyl) and a Regiorandom Isopolymer: Ni vs Pd Catalysis of 2(5)-Bromo-5(2)-(bromozincio)-3-hexylthiophene Polymerization. *J. Am. Chem. Soc.* **1992**: *114*, 10087-10088.

13.Chen, T.–A.; O'Brien, R. A.; Rieke, R. D. Use of Highly Reactive Zinc Leads to a New, Facile Synthesis for Polyarylenes. *Macromolecules* **1993**: *26*, 3462-3463.

14. Wu, X.; Chen, T.–A.; Rieke, R. D. Synthesis of Regioregular Head-to-Tail Poly[3-(alkylthio)thiophenes]. A Highly Electroconductive Polymer. *Macromolecules* **1995**: *28*, 2101-2102.

15. McCullough, R. D.; Lowe, R. D. Enhanced Electrical Conductivity in Regioselectively Synthesized Poly(3-alkylthiophenes). *J. Chem. Soc., Chem. Commun.* **1992**: 70-72.

16. Robert, S.; Lowe, P. C.; Ewbank, J. L.; Lei, Z.; McCullough, R. D. Regioreguler, Head-to-Tail Coupled Poly(3-alkylthiophenes) Made Easy by the GRIM Method: Investigation of the Reaction and the Origin of Regioselectivity. *Macromolecules* **2001**: *34*, 4324-4333.

17. McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. Design, Synthesis, and Control of Conducting Polymer Architectures: Structurally Homogeneous Poly(3-alkylthiophenes). *J. Org. Chem.* **1993**: *58*, 904-912.

18. McCullough, R. D.; Stephanie, T.–N.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. Self-Orienting Head-to-Tail Poly(3-alkylthiophenes): New Insights on Structure – Property Relationships in Conducting Polymers. *J. Am. Chem. Soc.* **1993**: *115*, 4910-4911.

19. McCullough, R. D.; Williams, S. P. Toward Tuning Electrical and Optical Properties in Conjugated Polymers Using Side Chains: Highly Conductive Head-to-Tail Heteroatom-Functionalized Polythiophenes. *J. Am. Chem. Soc.* **1993**: *115*, 11608-11609.

20. McCullough, R. D.; Williams, S. P.; Tristram-Nagle, S.; Jayaraman, M.; Ewbank, P. C.; Miller, L. The First Synthesis and New Properties of Regioregular, Head-To-Tail Coupled Polythiophenes. *Synth. Met.* **1995**: *69*, 279-282.

21. Pham, C. V.; Macomber, R. S.; Mark, H. B.; Zimmer, H. Lithiation Reaction of 2,5-Dibromothiophene. ^{13}C NMR Spectra of 3-Substituted Derivatives. *J. Org. Chem.* **1984**: *49*, 5250-5253.

22. Maior, R. M. S.; Hinkelmann, K.; Eckert, K.; Wudl, F. Synthesis and Characterization of Two Regiochemically Defined Poly(dialkylbithiophenes): A Comparative Study. *Macromolecules* **1990**: *23*, 1268-1279.

23. McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. Design, Synthesis, and Control of Conducting Polymer Architectures: Structurally Homogeneous Poly(3-alkylthiophenes). *J. Org. Chem.* **1993**: *58*, 904-912.

24. (a) Yamamoto, T.; Oguro, D.; Kubota, K. Viscometric and Light Scattering Analyses of $CHCl_3$ Solutions of Poly(3-alkylthiophene-2,5-diyl)s. *Macromolecules* **1996**: *29*, 1833-1835.

(b) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. Effect of Molecular Weight on Spectroscopic and Spectroelectrochemical Properties of Regioregular Poly(3-hexylthiophene). *Macromolecules* **1998**: *31*, 5051-5058.

25. Heeger, A. J. Semiconducting and Metallic Polymers: the Fourth Generation of Polymeric Materials. *Synth. Met.* **2002**: *125*, 23-42.

26. Skotheim, T. A., ed. Handbook of Conducting Polymers. Marcel Dekker : New York, **1986**.

27. (a) Winor, M. J.; Wamsley, P.; Moulton, J.; Smith, P.; Heeger, A. J. Structural Evolution in Iodine-Doped Poly(3-alkylthiophenes). *Macromolecules* **1991**: *24*, 3812-3815.

(b) Tashiro, K.; Kobayashi, M.; Kawai, T.; Yoshino, K. Crystal Structural Change in Poly(3-alkylthiophene)s Induced by Iodine Doping as Studied by an Organized Combination of X-ray Diffraction, Infrared/Raman Spectroscopy and Computer Simulation Techniques. *Polymer* **1997**: *38*, 2867-2879.

(c) Wochnowski, C.; Metev, S. UV-Laser-Assisted Synthesis of Iodine-Doped Electrical Conductive Polythiophene. *Appl. Surf. Sci.* **2002**: *186*, 34-39.

28. (a) Ahlskog, K. Stability Studies on $AuCl_3$-doped Poly(3-hexylthiophene); Comparison with $FeCl_3$ Doping. *Synth. Met.* **1995**: *72*, 197-200.

(b) Meline, R. L.; Kasim, R. K.; Lu, W.–K.; Elsenbaumer, R. L. Poly(3-alkylthiophenes): Optimising Conductivity as a Function of Regioregularity, Dopant and Casting Solvent. *Synth. Met.* **1999**: *101*, 446.

29. Ciprelli, J.–L.; Clarisse, C.; Delabouglise, D. Enhanced Stability of Conducting Poly(3-octylthiophene) Thin Films using Organic Nitrosyl Compounds. *Synth. Met.* **1995**: *74*, 217-222.

30. Lebedev, M.; Lauritzen, M. V.; Curzon, A. E.; Holdcroft, S. Solvato-Controlled Doping of Conducting Polymers. *Chem. Mater.* **1998**: *10*, 156-163.

31. Zen, A.; Saphiannikova, M.; Neher D.; Asawaripom, U.; Scherf, U. Comparative Study of the Field-Effect Mobility of a Copolymer and a Binary Blend Based on Poly(3-alkylthiophene). *Chem. Mater.* **2005**: *17*, 781-786.

32. Groenendaal, L.; Jonas, F.; Freitag. D.; Pielartzik, H.; Reynolds, R. Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future. *Adv. Mater.* **2000**: *12*, 481-494.

33. Meng, H.; Perepichka, D. F.; Bendikov, M; Wudl, F.; Pan, G. Z.; Yu, W.; Dong, W.; Brown, S. Solid-state synthesis of conducting polythiophene via an unprecedented heterocyclic coupling reaction. *J. Am. Chem. Soc.* **2003**: *125*, 15151.

APPENDICES

APPENDIX A

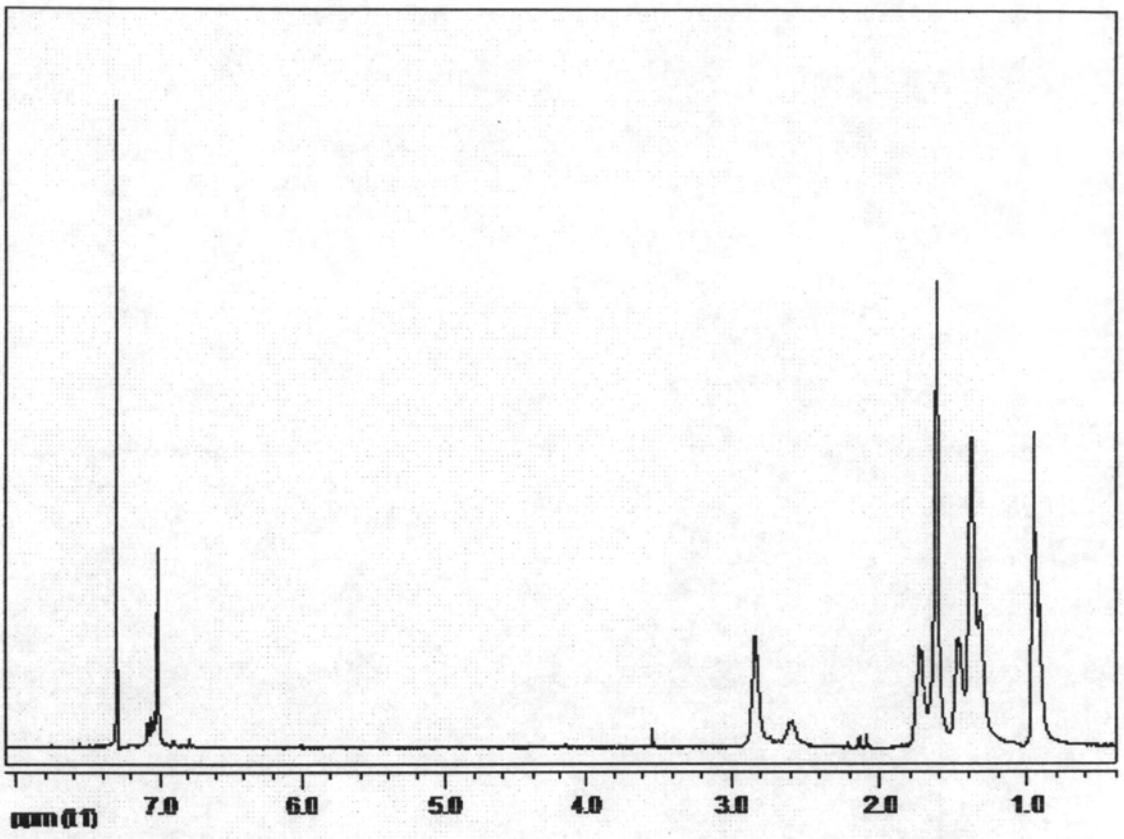

Figure A-1 The ^{1}H-NMR (400 MHz, $CDCl_3$) of poly(3-hexylthiophene)

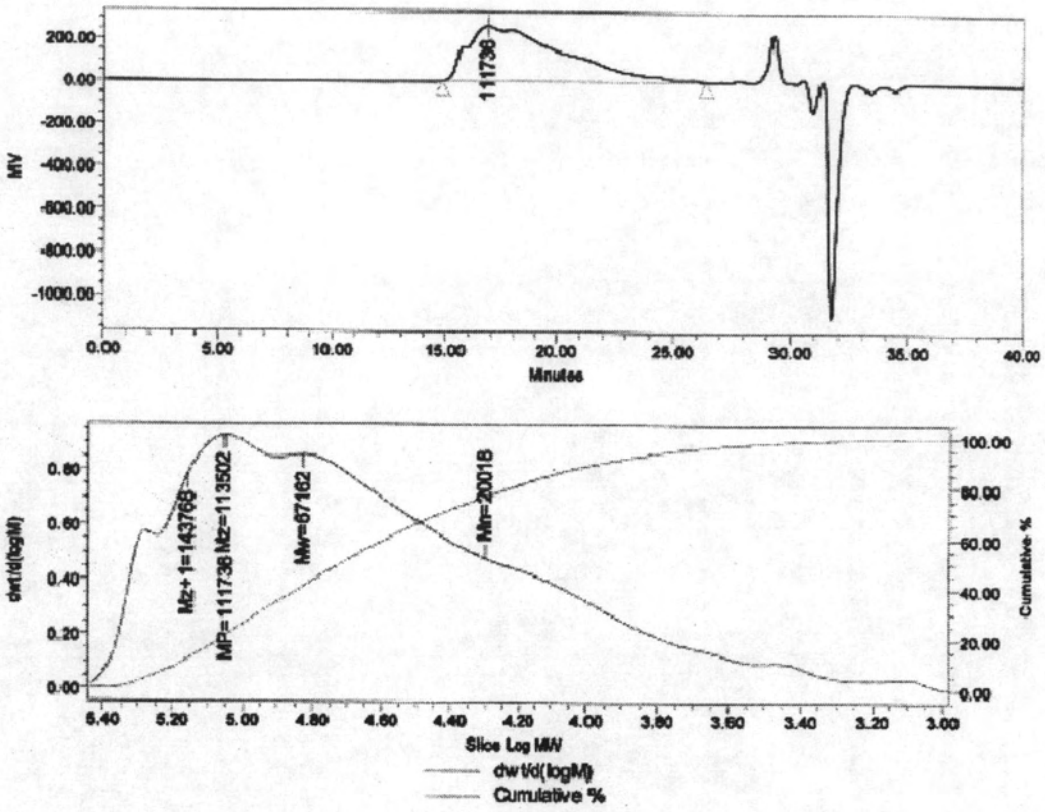

Figure A-2 GPC spectra of P3HT from mole ratio of 3-hexylthiophene to ferric chloride equals 1 : 3 using dichloromethane as solvent

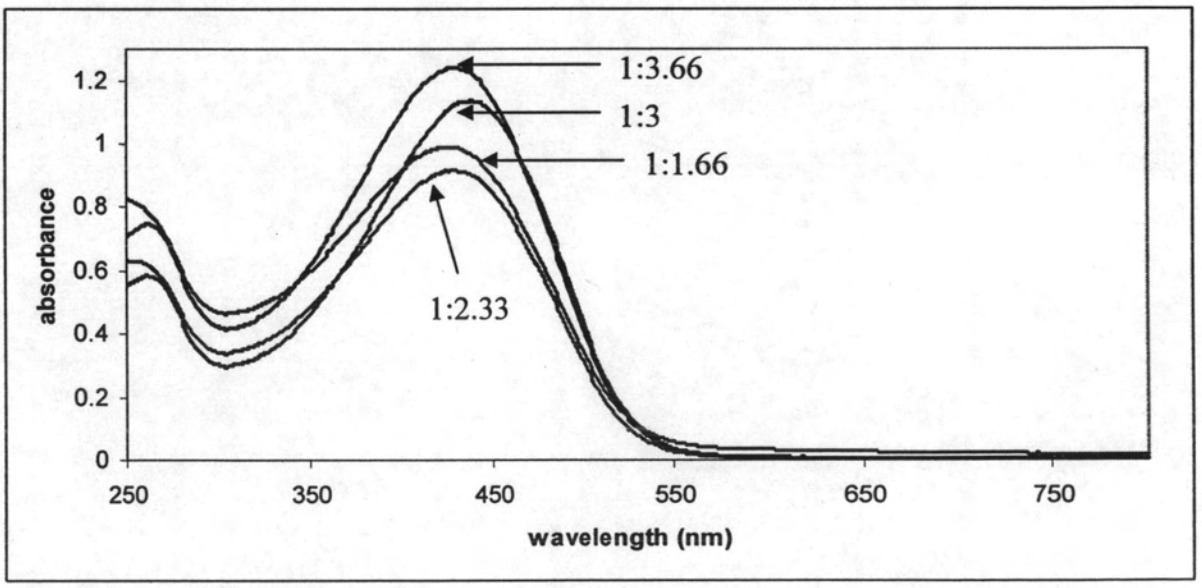

Figure A-3 UV-visible spectra of P3HT prepared from various ratios of starting material at room temperature (section 3.1.1, the spectra are not quantitatively scaled)

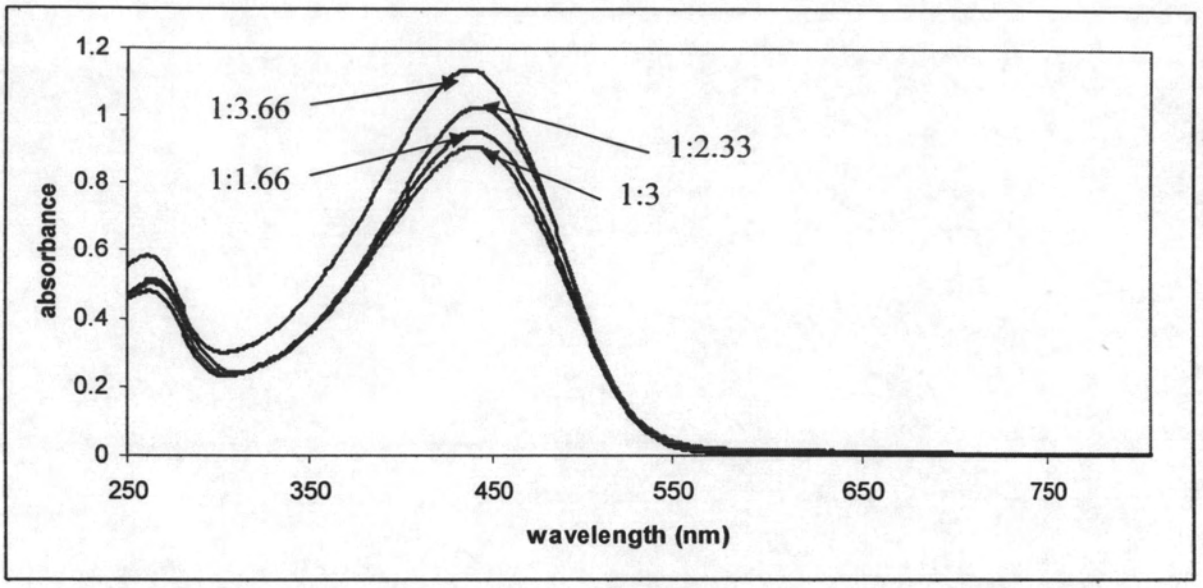

Figure A-4 UV-visible spectra of P3HT prepared from various ratios of starting material at -22 °C (section 3.1.2, the spectra are not quantitatively scaled)

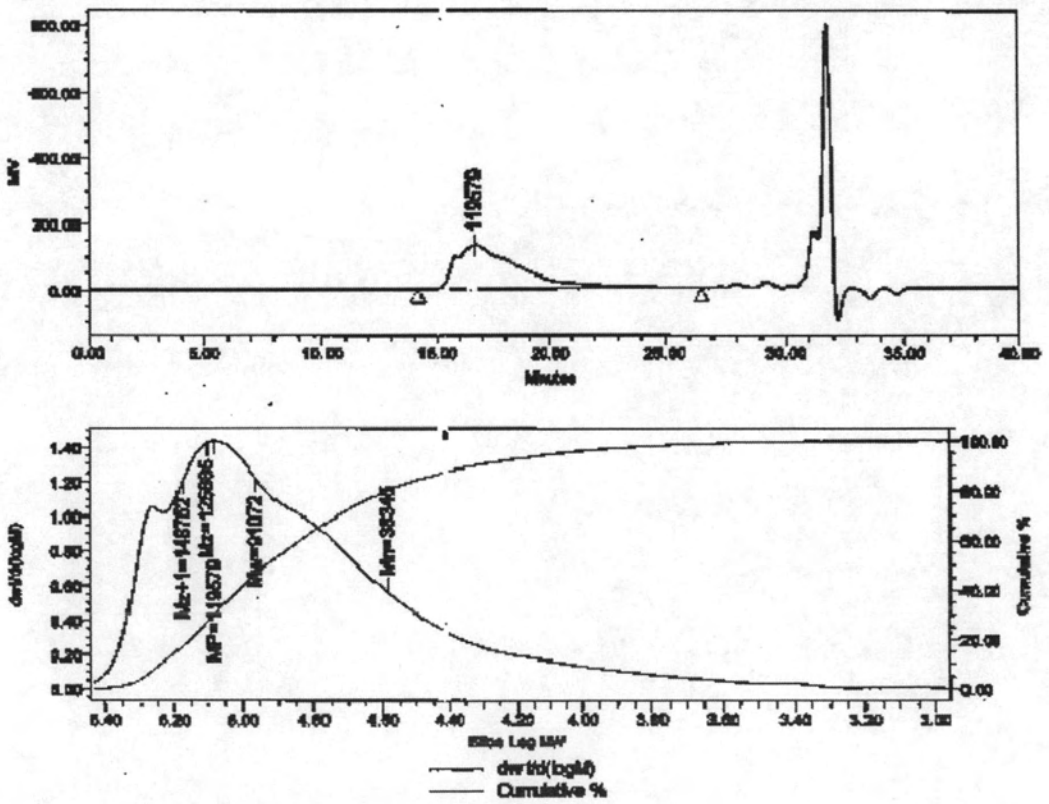

Figure A-5 GPC spectra of P3HT from mole ratio of 3-hexylthiophene to ferric chloride equals 1 : 2.33

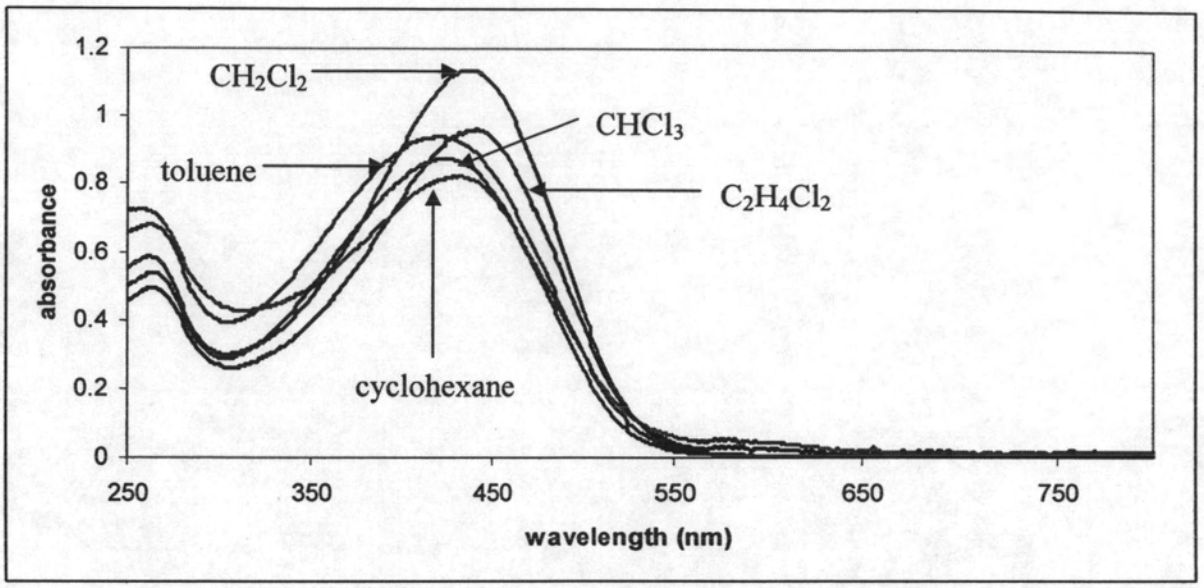

Figure A-6 UV-visible spectra of P3HT prepared in a variety of solvent

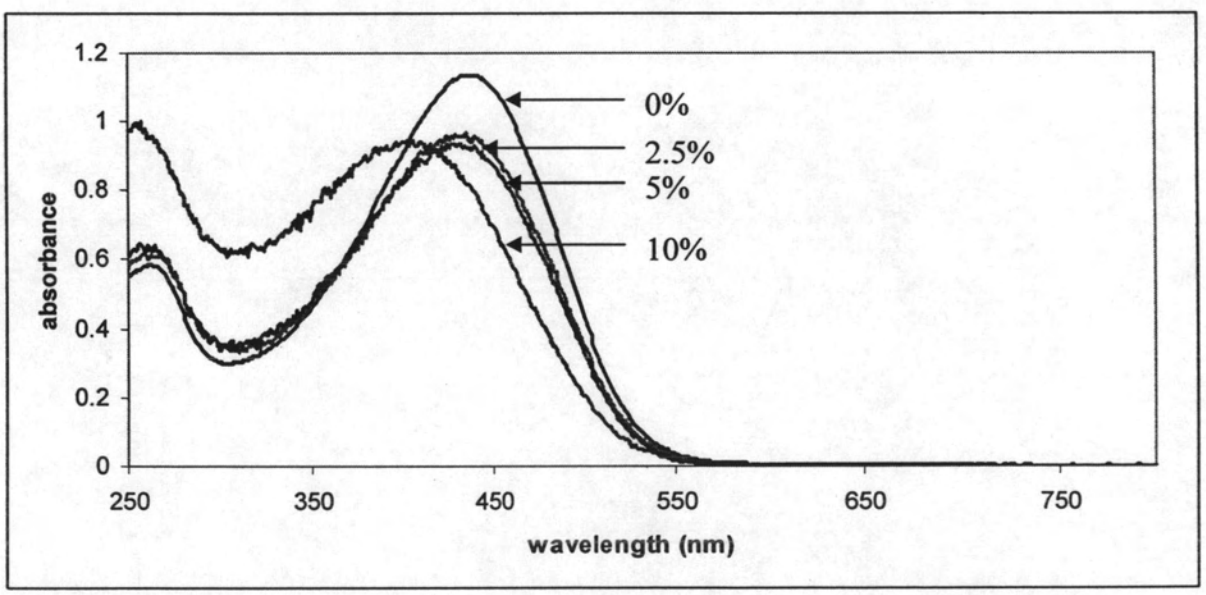

Figure A-7 UV-visible spectra of P3HT obtained from the reactions with added water

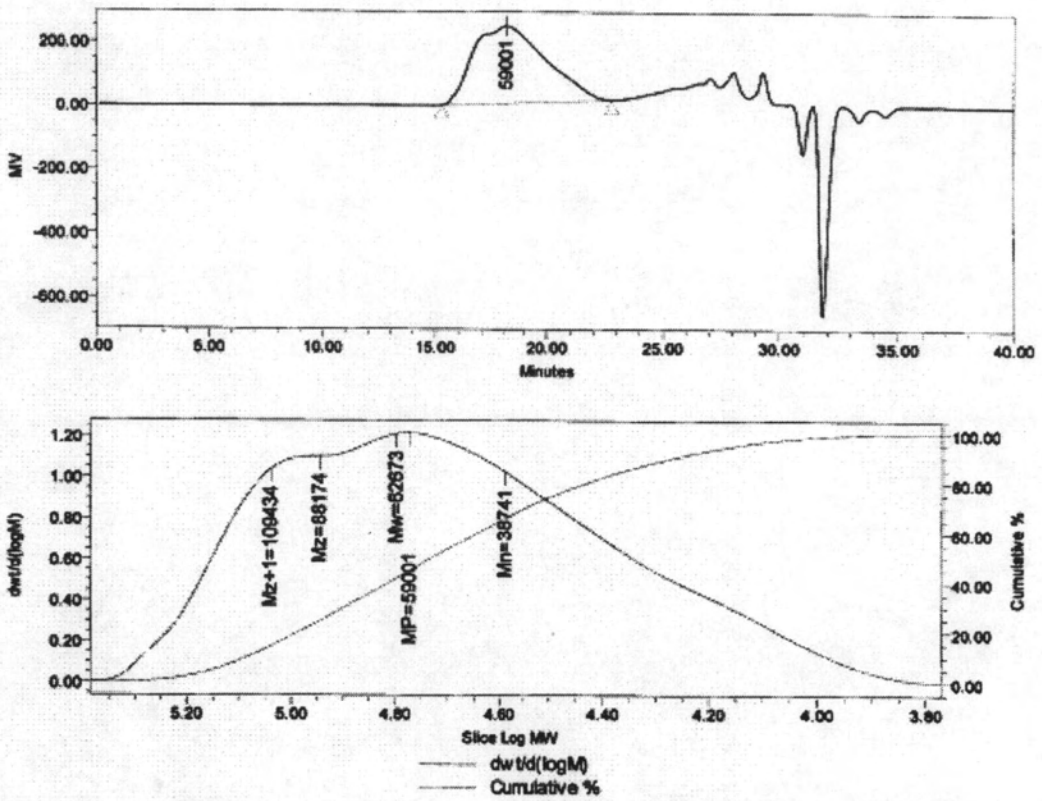

Figure A-8 GPC spectra of dichloromethane fraction of P3HT prepared from mole ratio of 3-hexylthiophene to ferric chloride equals 1 : 3

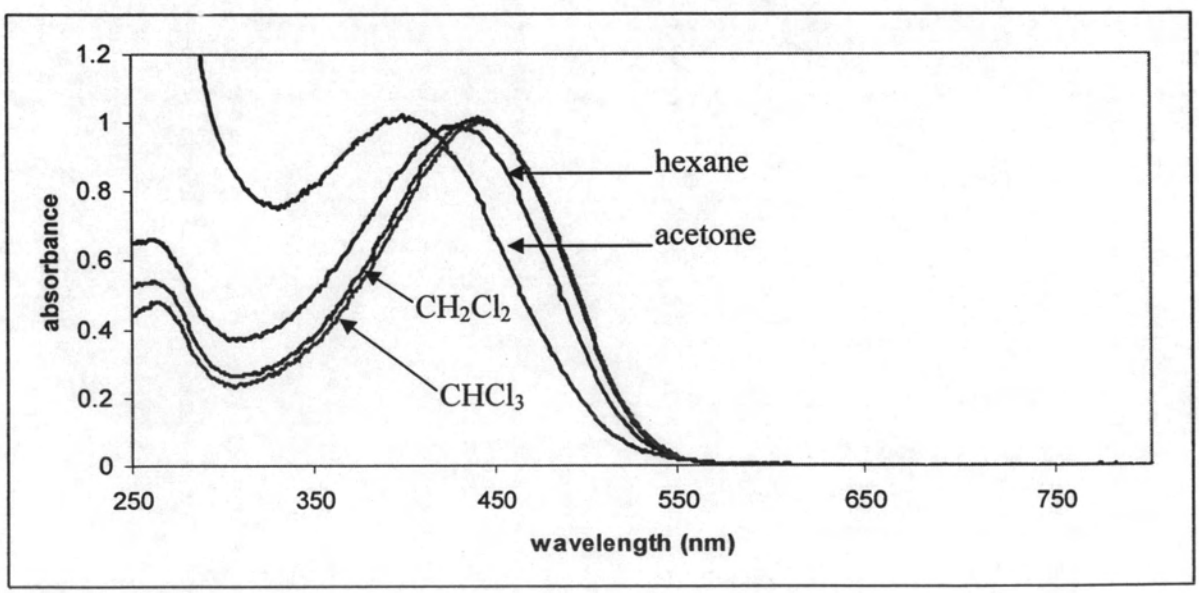

Figure A-9 UV-visible spectra of P3HT fractions from consecutive extractions

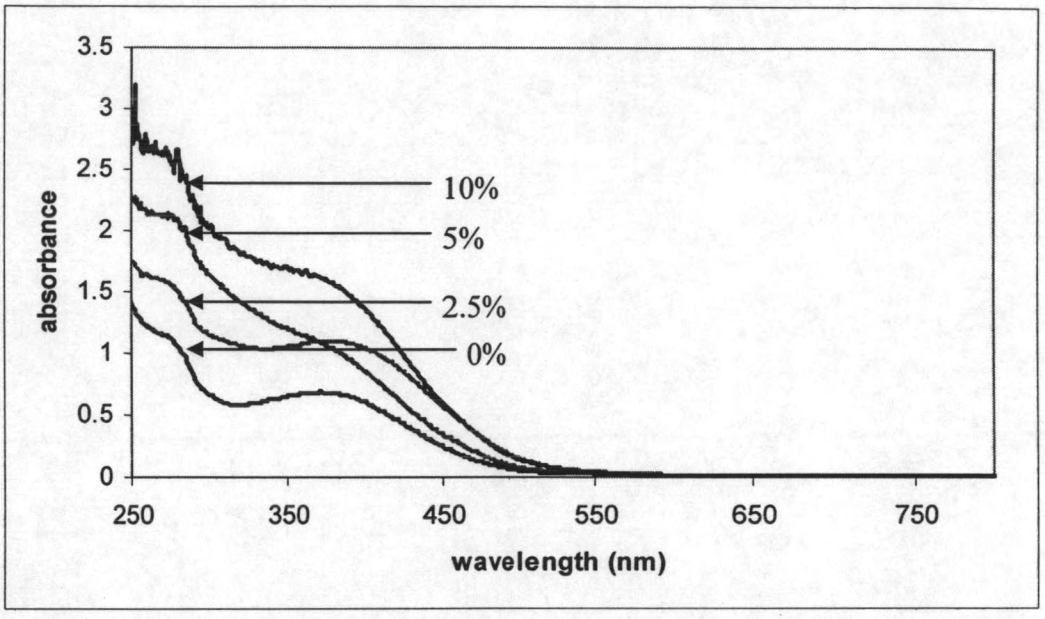

Figure A-10 UV-visible spectra of acetone fractions of P3HT obtained from the reactions with various percentage of added water

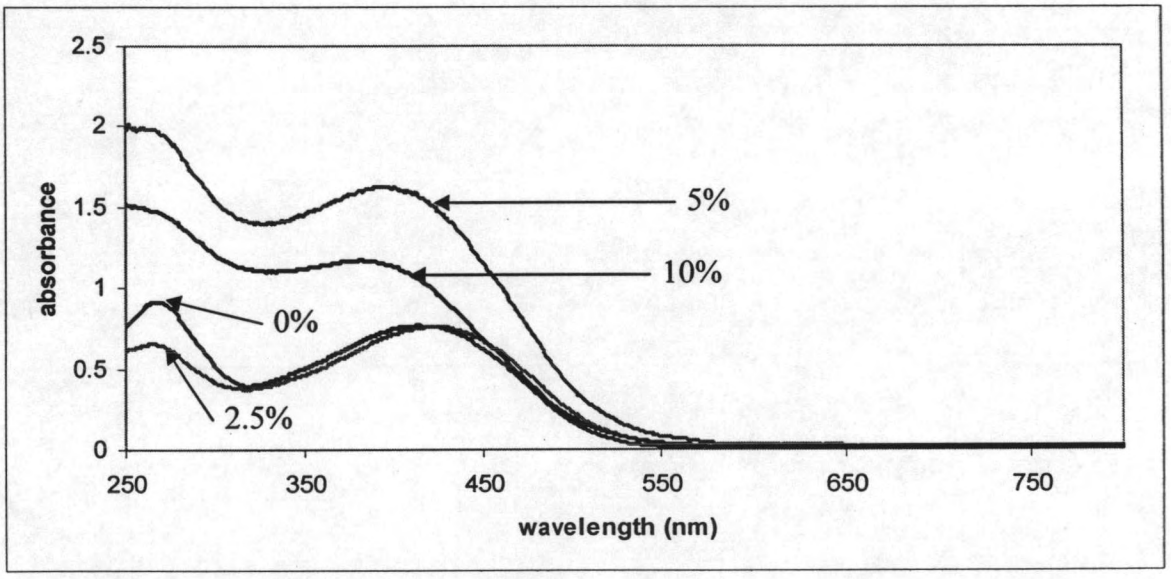

Figure A-11 UV-visible spectra of hexane fractions of P3HT obtained from the reactions with various percentage of added water

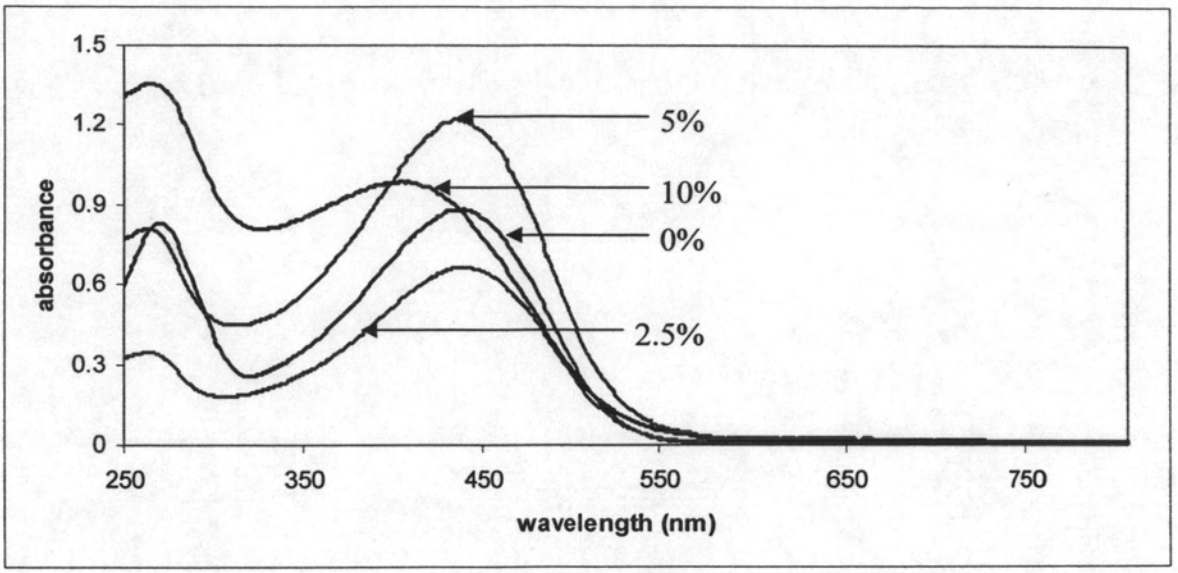

Figure A-12 UV-visible spectra of dichloromethane fractions of P3HT obtained from the reactions with various percentage of added water

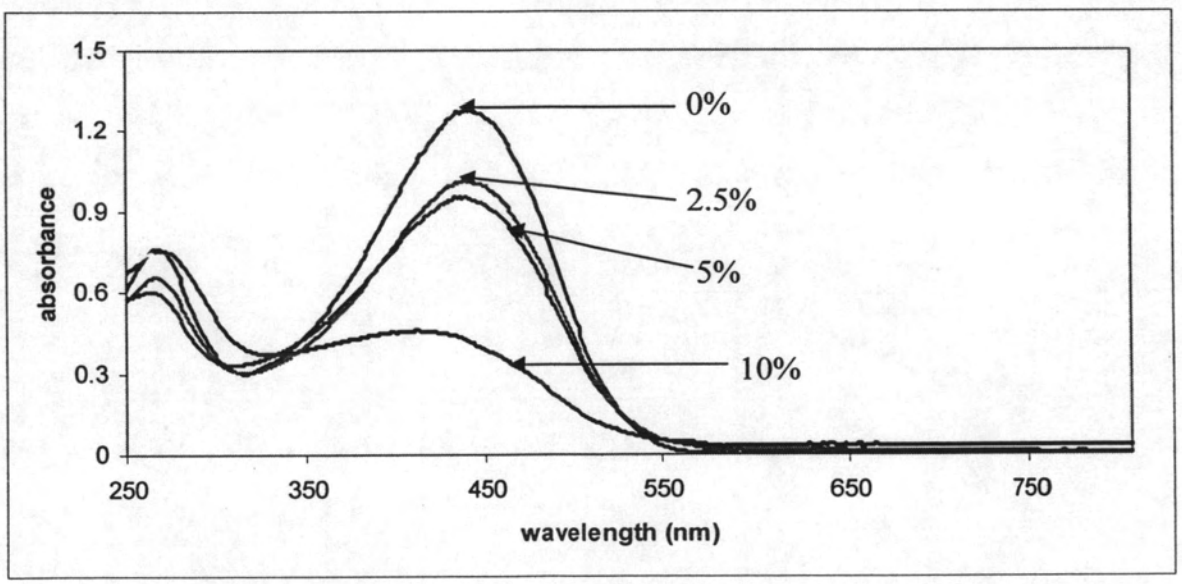

Figure A-13 UV-visible spectra of chloroform fraction of P3HT obtained from the reactions with various percentage of added water

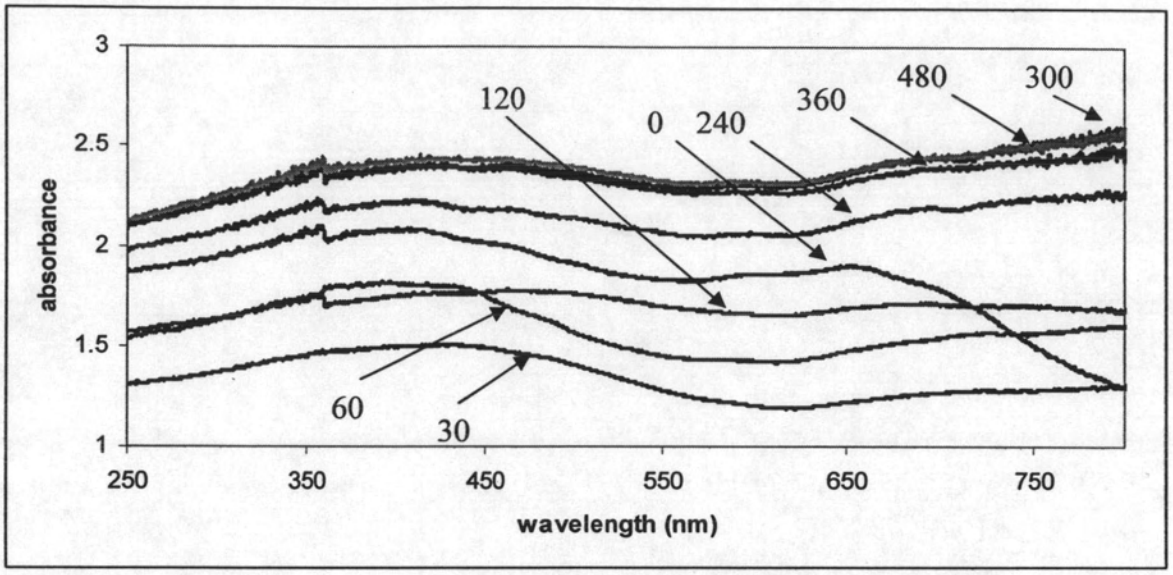

Figure A-14 UV-visible spectra of 120 µmol of P3HT doped by TCA (µmol)

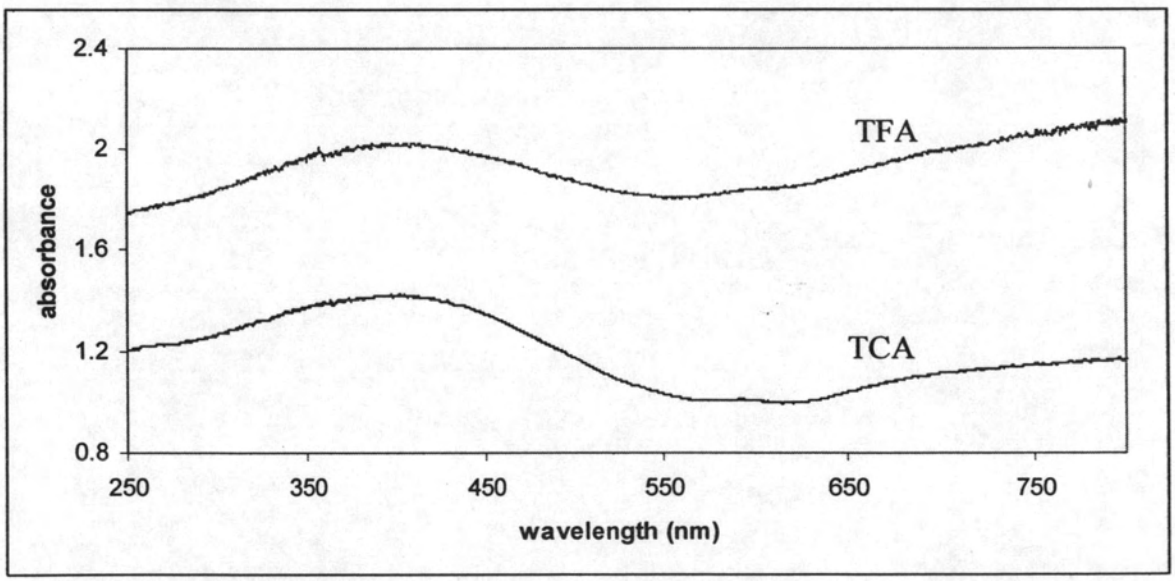

Figure A-15 UV-visible spectra of 120 µmol of P3HT doped by TCA and TFA at 120 µmol

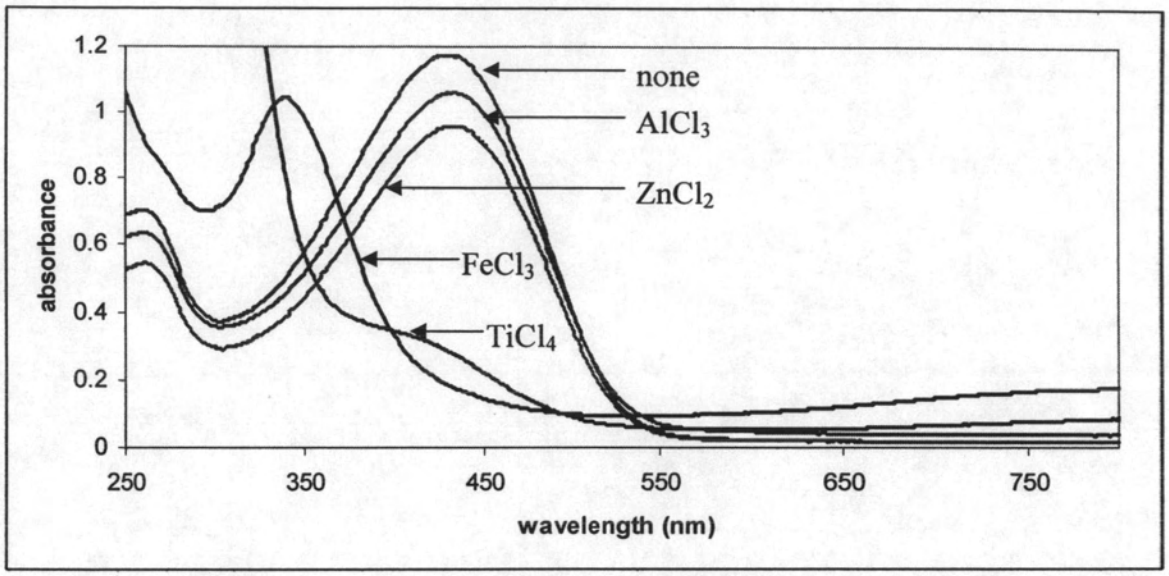

Figure A-16 UV-visible spectra of P3HT doped by Lewis acids

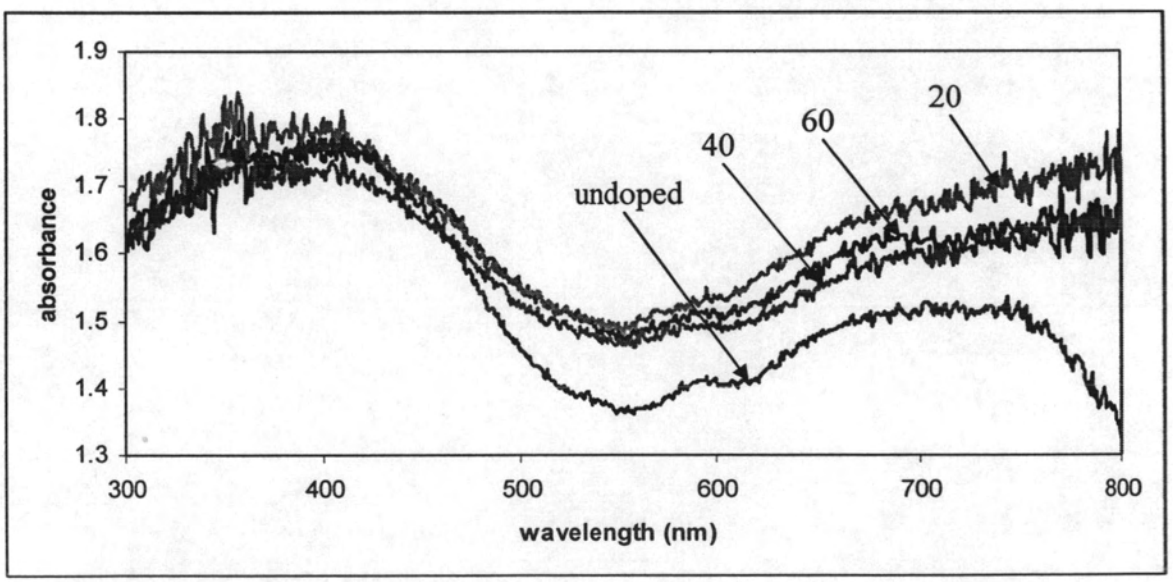

Figure A-17 UV-visible spectra of P3HT film doped by MSA at various doping time (min)

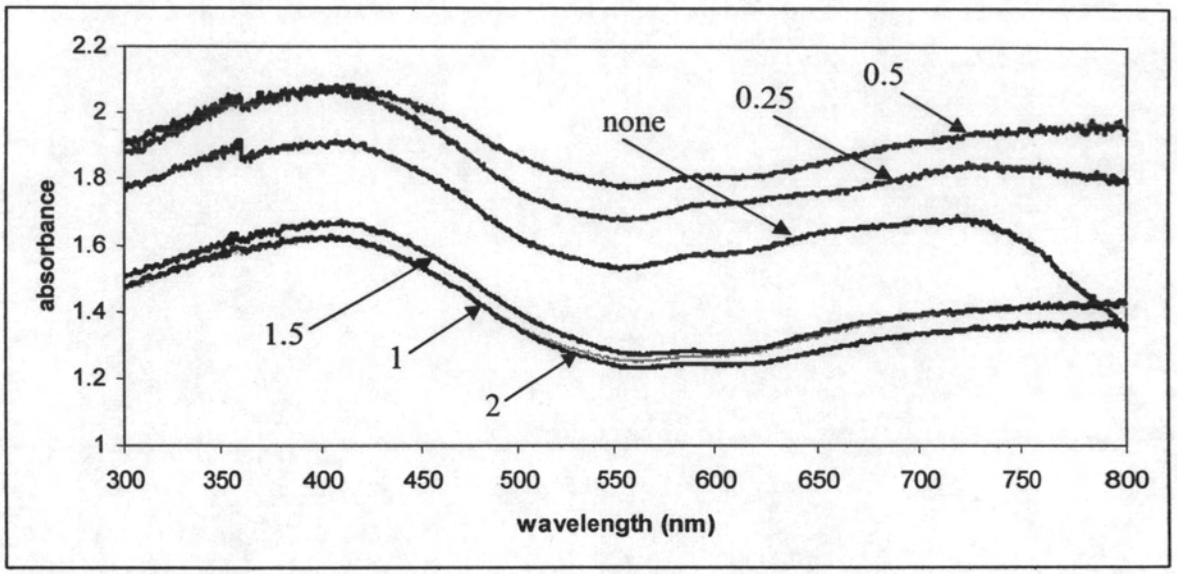

Figure A-18 UV-visible spectra of P3HT solvato-controlled doped by various mole ratios of MSA and thiophene

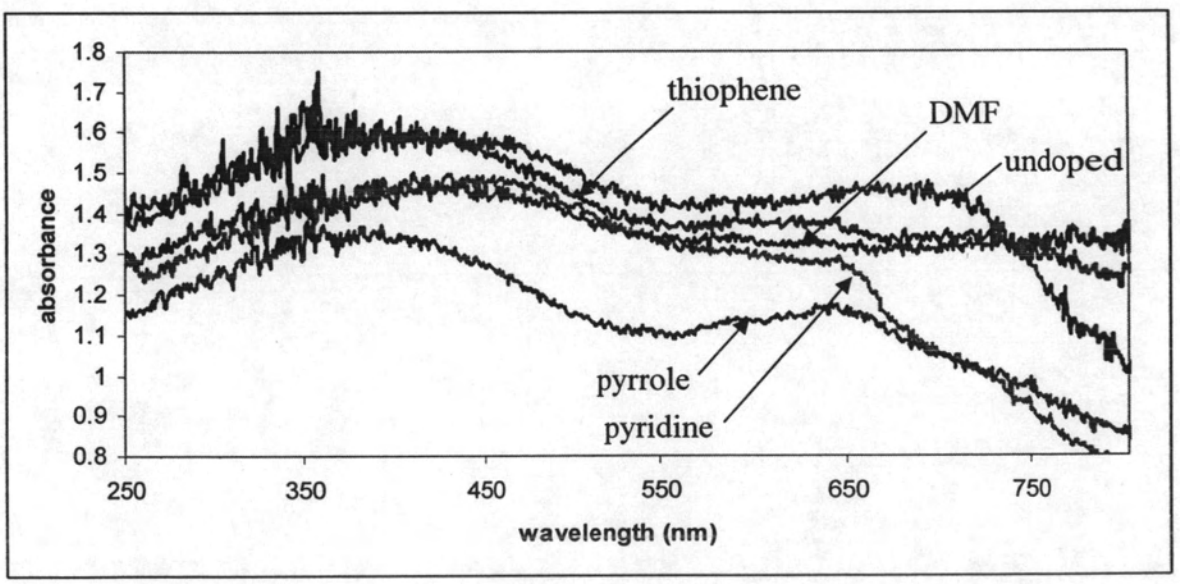

Figure A-19 UV-visible spectra of P3HT solvato-controlled doped by MSA with various bases

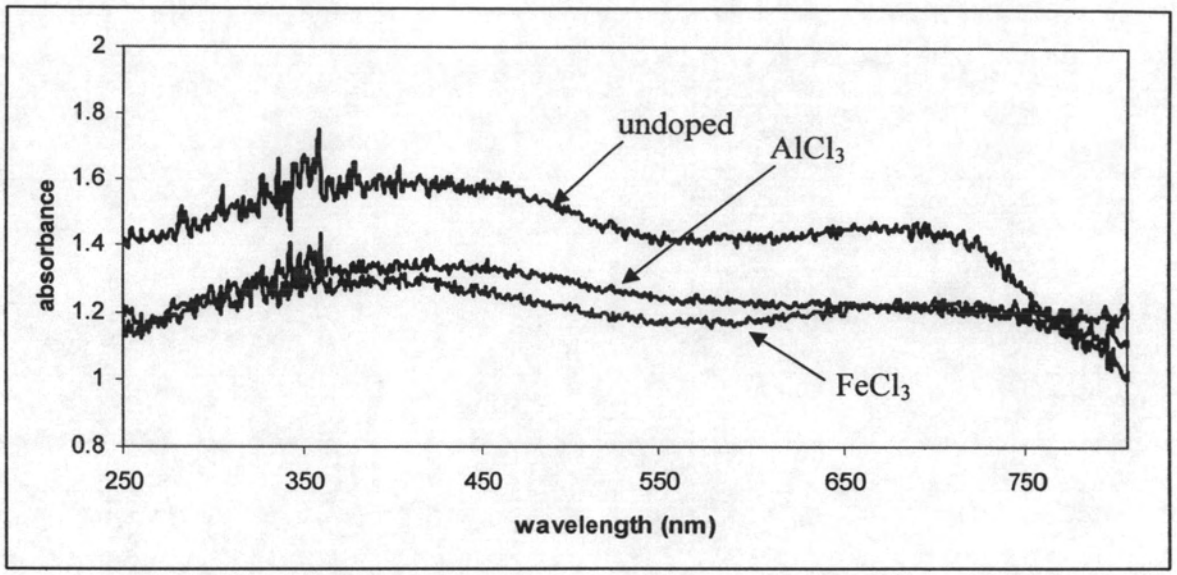

Figure A-20 UV-visible spectra of P3HT solvato-controlled doped by $AlCl_3$ and $FeCl_3$ with pyridine

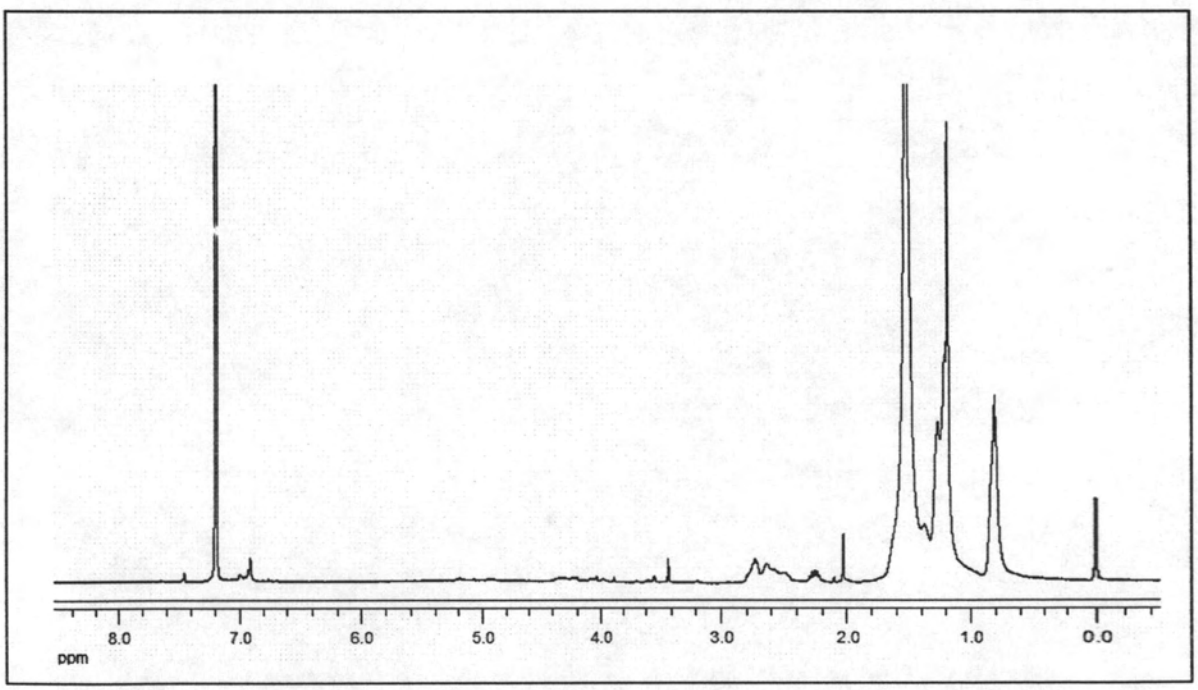

Figure A-21 The ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of the copolymer of 3-hexylthiophene and EDOT (mole ratio of 3-hexylthiophene:EDOT equals 0.75:0.25)

APPENDIX B

Example of the calculation of AC-index

From UV-Visible spectroscopy data;

λ (nm)	Absorbance	λ_i	A_i	$\lambda_i A_i$
		(λ1+λ2)/2	(A1+A2)/2	
250.0	1.865	250.05	1.865	466.3433
250.1	1.865	250.15	1.8655	466.5398
250.2	1.866	250.25	1.866	466.9665
250.3	1.866	250.35	1.8665	467.1531
250.4	1.867	250.45	1.867	467.5902
250.5	1.867	250.55	1.8685	467.7769
250.6	1.870	250.65	1.8705	468.7155
250.7	1.871	250.75	1.872	469.1533
250.8	1.873	250.85	1.872	469.8421
250.9	1.871	250.95	1.87	469.5275
251.0	1.879	-	-	-
Sum (250-251 nm)		**-**	**18.683**	**4679.598**

$$\text{AC-index (250-251 nm)} = \frac{\Sigma\lambda_i A_i}{\Sigma A_i} = \frac{4675.598}{18.683} = \mathbf{250.26}$$

Example of the calculation of %HT

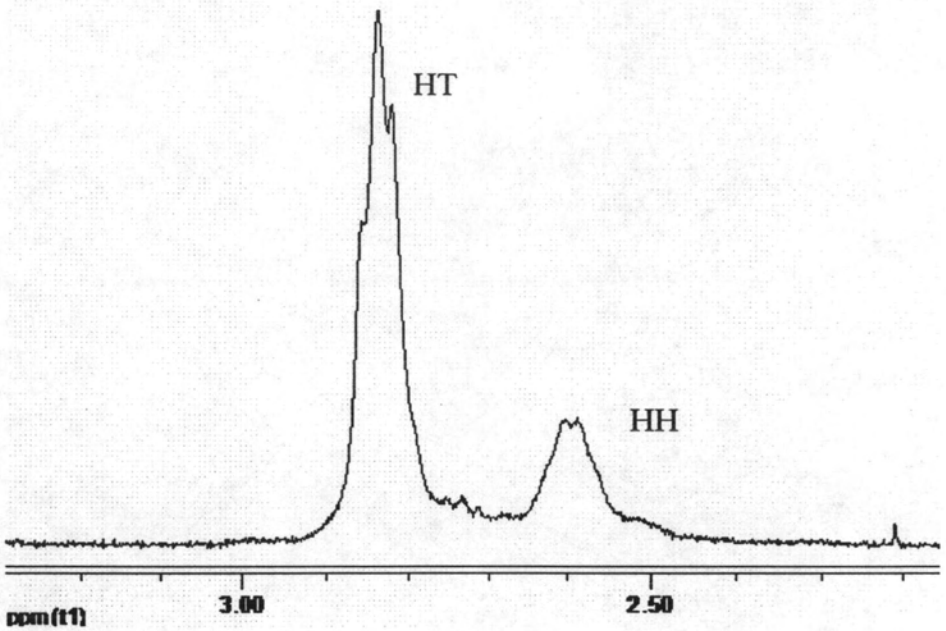

Figure B-1 Part of ^{1}H NMR spectrum data of P3HT

From ^{1}H NMR spectral data of P3HT from various mole ratios of 3-hexylthiophene:$FeCl_3$

Mole ratios of 3-hexylthiophene:$FeCl_3$	**HT** Area	**HH** Area	%HT
1 : 1.66	1.00	0.26	79
1 : 2.33	1.00	0.28	78
1 : 3.00	1.00	0.28	78
1 : 3.66	1.00	0.33	75

Example of the calculation of %HT of the mole ratios of 3-hexylthiophene:$FeCl_3$ equals 1 : 1.66

$$\%HT = \frac{\textbf{HT} \text{ Area}}{\textbf{HT} \text{ Area} + \textbf{HH} \text{ Area}} \times 100 = \frac{1.00}{1.26} \times 100 = \mathbf{79}$$

Calculation of %EDOT in the copolymer of 3-hexylthiophene and EDOT

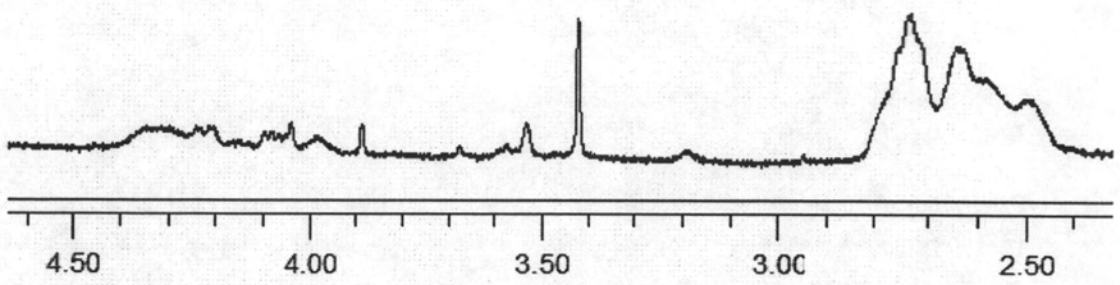

Figure B-2 Part of ^{1}H NMR spectrum of the copolymer of 3-hexylthiophene and EDOT

ratio by peak areas of

3-hexylthiophene (α-CH_2, 2.45-2.8 ppm) : EDOT(-OCH_2CH_2O-, 3.9-4.4 ppm)

= 1:0.0864

weight of 3-hexylthiophene

$$= \frac{1\times\text{MW of 3-hexylthiophene}}{(1\times\text{MW of 3-hexylthiophene})+(0.0864\times\text{MW of EDOT})}$$

$$= \frac{1\times166.2842}{(1\times166.2842)+(0.0864\times140.1342)} = 0.9321$$

weight of EDOT

$$= \frac{0.0864\times\text{MW of EDOT}}{(1\times\text{MW of 3-hexylthiophene})+(0.0864\times\text{MW of EDOT})}$$

$$= \frac{0.0864\times140.1342}{(1\times166.2842)+(0.0864\times140.1342)} = 0.0678$$

ratio by weight of 3-hexylthiophene : EDOT = 0.9321:0.0678

percentage of 3-hexylthiophene : EDOT in polymer chain = 93.21:6.78

APPENDIX C

Table C-1 AC-index of P3HT doped by various amount of TCA

P3HT (μmol)	TCA (μmol)	AC-index
120	0	512
120	30	517
120	60	518
120	120	525
120	240	527
120	300	530
120	360	528
120	480	529

Table C-2 AC-index of P3HT doped by TCA and TFA

P3HT (μmol)	Doping agent (120 μmol)	AC-index
120	TCA	525
120	TFA	528

Table C-3 AC-index of P3HT doped by MSA at surface

Doping time (min)	AC-index
0	541.27
20	546.8
40	547.12
60	547.87

Table C-4 Solvato-controlled doping of P3HT : MSA : thiophene = 1 : X : 2

X	AC-index
0	541.05
0.25	543.99
0.5	547.02
1	544.31
1.5	542.92
2	543.16

X = mole ratio of MSA

Table C-5 Solvato-controlled doping of P3HT by MSA and bases

Bases	AC-index
none	504
Pyridine	522
Pyrrole	528
Thiophene	538
DMF	546

Table C-6 Solvato-controlled doping of P3HT by $AlCl_3$ and $FeCl_3$ using pyridine as a ligand

Types of ligand	AC-index
none	532
$AlCl_3$	542
$FeCl_3$	548

VITA

Miss Ketthip Anuwareephong was born on October 30, 1981 in Bangkok, Thailand. She received a Bachelor degree of Science from Department of Chemistry, Faculty of Science, Kasetsart University, Thailand in 2004. She was admitted to a Master's Degree Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2004 and completed the program in 2006. Her address is 797/165 Soi Sutthiporn, Prachasongkhro Road, Dindang, Bangkok 10400.