

REFERENCES

1. (a) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578. (b) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, 39, 1098.
2. Nalwa, H. S., ed. "Handbook of Organic Conductive Molecules and Polymers: Vol. 4. Conductive Polymers: Transport, Photophysics and Applications" John Wiley & Sons: Chichester, **1997**.
3. Wallace, G. G.; Spinks, G. M.; Kane-Magure, L. A. P.; Teasdale, P. R. "Conductive Electroactive Polymer; Intelligent Materials Systems" CRC Press: Washington D.C. **2003**.
4. Schlesinger, M.; Paunovic, M. "Modern Electroplating" John Wiley & Sons: Chichester, **1997**.
5. Margolis, J. M. "Conductive Polymer and Plastic" Chapman and Hall: London, **1989**.
6. Nalwa, H. S., ed. "Handbook of Organic Conductive Molecules and Polymers: Vol. 2. Conductive Polymers: Synthesis and Electrical Properties" John Wiley & Sons: Chichester, **1997**.
7. Mullekom, H. A. M. "The Chemistry of High and Low Band Gap Conjugated Polymers" Ph.D. Dissertation, Eindhoven University of Technology, the Netherlands, **2000**.
8. <http://www.nobel.se/chemistry/laureates/2000/chemadv.pdf>
9. <http://homepage.dtn.ntl.com/colin.pratt/home.html>

10. Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. "Synthesis and properties of the Longest Oligothiophenes: The Icosamer and Heptacosamer" *J. Org. Chem.* **1998**, *63*, 8632-8633.
11. Nalwa, H. S., ed. "Handbook of Organic Conductive Molecules and Polymers: Vol. 3. Conductive Polymers: Spectroscopy and Physical Properties" John Wiley & Sons: Chichester, **1997**.
12. Roncali, J. "Conjugated Poly(thiophene): Synthesis, Functionalization, and Applications" *Chem. Rev.* **1992**, *92*, 711.
13. 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.
14. McCullough, R. D.; Tristram-Nagle, S.; 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.
15. Sato, M.; Morii, H. "Nuclear Magnetic Resonance Studies on Electrochemically Prepared Poly(3-dodecylthiophene)" *Macromolecules* **1991**, *24*, 1196-1200.
16. Meline, R. L.; Kasim, R. K.; Lu, W.; Elsenbaumer, R. L. "Poly(3-alkylthiophene): Optimising Conductivity as Function of Regioregularity, Dopant and Casting Solvent" *Synth. Met.* **1999**, *101*, 446.
17. (a) Barbarella, G.; Zambianchi, M.; Toro, R. D.; Colonna, M. J.; Iarossi, D.; Bongini, A. "Regioselective Oligomerisation of 3-(Alkylsulfanyl)thiophenes with Ferric Chloride" *J. Org. Chem.* **1996**, *61*, 8285-8292. (b) McCarley, T. D.; Noble, C. O.; DuBois, C. J., Jr.; McCarley, R. L. "MALDI-MS Evaluation of Poly(3-hexylthiophene)

Synthesized by Chemical Oxidation with FeCl_3 ” *Macromolecules* **2001**, *34*, 7999-8004.

18. Corradi, R.; Armes, S. P. “Chemical Synthesis of Poly(3,4-ethylenedioxythiophene)” *Synth. Met.* **1997**, *84*, 453-454.
19. Pei, Q.; Zuccarello, G.; Ahlshog, M.; Inganas, O. “Electrochromic and Highly Stable Poly(3,4-ethylenedioxythiophene) Switches between Opaque Blue-Black and Transparent Sky Blue” *Polymer* **1994**, *35*, 1347-1351.
20. Yassar, A.; Roncali, J.; Garnier, F. “Conductivity and Conjugation Length in Poly(3-methylthiophene) Thin Films” *Macromolecules* **1989**, *22*, 804-809.
21. Wu, X.; Chen, T.; Rieke, R. D. “Synthesis of Regioregular Head-to-Tail Poly[3-(alkylthio)thiophene]. A Highly Electroconductive Polymer” *Macromolecules* **1995**, *28*, 2101-2102.
22. <http://www.sdu.dk/Nat/Chem/research/molspec/pcs/copol.htm>
23. Chen, T.; 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.
24. 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 Polythiophene” *Synth. Met.* **1995**, *69*, 279-282.
25. Yassar, A.; Roncali, J.; Garnier, F. “Conductivity and Conjugation Length in Poly(3-methylthiophene) Thin Films” *Macromolecules* **1989**, *22*, 804-809.
26. Pomerantz, M.; Liu, M. L. “Synthesis and Properties of Poly[3-(ω -bromoalkyl)thiophene]” *Synth. Met.* **1999**, *101*, 95.

27. Wu, X.; Chen, T.; Rieke, R. D. "A Study of Small Band Gap Polymer: Head to Tail Regioregular Poly[3-(alkylthio)thiophene] prepared by Regioselective Synthesis Using Active Zinc" *Macromolecules* **1996**, *29*, 7671-7677.
28. Masuda, H.; Asano, D. K.; Kaeriyama, K. "Synthesis of Poly(3-alkoxymethylthiophenes)" *Synth. Met.* **1999**, *101*, 73-74.
29. Zotti, G.; Zecchin, S.; Schiavon, G. "Conductive and Magnetic Properties of 3,4-Dimethoxy- and 3,4-Ethylenedioxy-Capped Polypyrrole and Polythiophene" *Chem. Mater.* **2000**, *12*, 2996-3005.
30. Buvat, P.; Hourquebie, P. "Metallic Properties of Polythiophene Based Conducting Polymers" *Synth. Met.* **1999**, *101*, 17-18.
31. Groenendaal, L.; Zotti, G.; Jonas, F. "Optical, Conductive and Magnetic Properties of Electrochemically prepared Alkylated Poly(3,4-ethylenedioxythiophene)s" *Synth. Met.* **2001**, *118*, 105-109.
32. Bakhshi, A. K. "Ab Initio Study of the Electronic Structure and Conduction Properties of Oxy-Derivatives of Polythiophene" *Solid State Commun.* **1995**, *94*, 943-946.
33. Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Antolini, L.; Pudova, O.; Bongini, A. "Oligothiophene *S,S*-dioxides. Synthesis and Electronic Properties in Relation to the Parent Oligothiophenes" *J. Org. Chem.* **1998**, *63*, 5497-5506.
34. Barbarella, G.; Pudova, O.; Arbizzani, C.; Mastragostino, M.; Bongini, A. "Oligothiophene-*S,S*-dioxides: a New Class of Thiophene-Based Materials" *J. Org. Chem.* **1998**, *63*, 1742-1745.
35. Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M. "Controlling the Electronic Properties of Polythiophene through the Insertion of

Nonaromatic Thienyl *S,S*-dioxide Units” *Chem. Mater.*, **1999**, *11*, 2533-2541.

36. (a) Barbarella, G.; Favaretto, L.; Zambianchi, M.; Pudova, O.; Arbizzani, C.; Bongini, A.; Mastragostino, M. “From Easily Oxidized to Easily Reduced Thiophene-Based Materials” *Adv. Mater.* **1998**, *10*, 551-554. (b) Bongini, A.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Mastragostino, M.; Arbizzani, C.; Soavi, F. “New n-Dopable Thiophene Based Polymers” *Synth. Met.* **1999**, *101*, 13-14.
37. Arbizzani, C.; Barbarella, G.; Bongini, A.; Favaretto, L.; Mastragostino, M.; Ostoja, P.; Pudova, O.; Zambianchi, M. “Oligothiophene *S,S*-Dioxides: Towards n-type Semiconductor Oligothiophenes” *Opt. Mater.* **1998**, *9*, 43-45.
38. Arbizzani, C.; Mastragostino, M.; Soavi, F. “Polythiophene *S,S* Dioxides: an Investigation on Electrochemical Doping” *Electrochim. Acta.* **2000**, *45*, 2273-2278.
39. Yamamoto, T.; Nurulla, I.; Hayashi, H.; Koinuma, H. “Conjugated Polymers Containing Thiophene-1,1-dioxide-2,5-diyl Unit in the Main Chain” *Synth. Met.* **1999**, *107*, 137-141.
40. Holdcroft, S. “A Photochemical Study of Poly(3-hexylthiophene)” *Macromolecules* **1991**, *24*, 4834-4838.
41. Oyama, T.; Naka, K.; Chujo, Y. “Polymer Homologue of DMSO: Synthesis of Poly(ethylene sulfoxide) by Selective Oxidation of Poly(ethylene sulfide)” *Macromolecules* **1999**, *32*, 5240-5242.
- 42 (a) Mock, W. A. “Stable Thiophene Sulfoxides” *J. Am. Chem. Soc.* **1970**, *92*, 7610. (b) Koyama, E.; Sanda, F.; Endo, T. “Radical Polyaddition of Dithiols with Diolefins Derived from Optically Active Amino Alcohols” *Macromolecules* **1998**, *31*, 1495-1500.

43. Allcock, H. R.; Olmeijer, D. L. "Polyphosphazenes Functionalized with Sulfone or Sulfoxide Groups: Synthesis, Characterization, and Possible Polymer Electrolyte Applications" *Macromolecules* **1998**, *31*, 8036-8046.
44. Brown, K. N.; Espenson, J. H. "Stepwise Oxidation of Thiophene and Its Derivatives by Hydrogen Peroxide Catalyzed by Methyltrioxorhenium(VII)" *Inorg. Chem.* **1996**, *35*, 7211-7216.
45. Gilman, H.; Nobis, J. F. "Rearrangement with 4-Iododibenzothiophene in Amination by Sodamide" *J. Am. Chem. Soc.* **1945**, 1479.
46. Block, E.; DeOrazio, R.; Thiruvazhi, M. "Simple Total Syntheses of Biologically Active Pentathiadecane Natural Products, 2,4,5,7,9-Pentathiadecane 2,2,9,9-Tetraoxide (Dysoxysulfone), from *Dysoxylum richii*, and 2,3,5,7,9-Pentathiadecane 9,9-Dioxide, the Misidentified Lenthionine Precursor SE-3 from Shiitake Mushroom (*Lentinus edodes*)" *J. Org. Chem.* **1994**, *59*, 2273-2275.
47. Caron, S.; Do, N. M.; Sieser, J. "A Practical, Efficient, and Rapid Method for the Oxidation of Electron Deficient Pyridines Using Trifluoroacetic Anhydride and Hydrogen Peroxide-Urea Complex" *Tetrahedron Lett.* **2000**, *41*, 2299-2302.
48. (a) Noureldin, N. A.; Zhao, D.; Lee, D. G. "Heterogeneous Permanganate Oxidation. 7. The Oxidation of Aliphatic Side Chains" *J. Org. Chem.* **1997**, *62*, 8767-8772. (b) Menger, F. M.; Lee, C. "Oxidation with Solid Potassium Permanganate" *J. Org. Chem.* **1979**, *44*, 3446-3448. (c) Shaabani, A.; Lee, D. G. "Solvent Free Permanganate Oxidations" *Tetrahedron Lett.* **2001**, *42*, 5833-5836.
49. (a) Murray, R. W.; Jeyaraman, R. "Dioxirane: Synthesis and Reactions of Methyl dioxiranes" *J. Org. Chem.* **1985**, *50*, 2847-2853. (b) Adam, W.; Curci, R.; Nunez, M. E. G.; Mello, R. "Thermally and Photochemically Initiated Radical Chain Decomposition of Ketone-Free

- Methyl(trifluoromethyl)dioxirane” *J. Am. Chem. Soc.* **1991**, *113*, 7654-7658. (c) Nakayama, J.; Nagasawa, H.; Sugihara, Y.; Ishii, A. “Synthesis, Isolation, and Full Characterization of the Parent Thiophene 1,1-Dioxide” *J. Am. Chem. Soc.* **1997**, *119*, 9077-9078. (d) González-Núñez, M. G.; Mello, R.; Royo, J.; Ríos, J. V.; Asensio, G. “Mechanism of the Oxidation of Sulfides by Dioxiranes. 1. Intermediacy of a 10-S-4 Hypervalent Sulfur Adduct” *J. Am. Chem. Soc.* **2002**, *124*, 9154-9163.
50. “The Aldrich Library of FT-IR Spectra” Milwaukee **1997**, *2*, 3466.
51. Leejarkpai, T. “Synthesis of Electrical Conducting Polymer by Solution Polymerisation” M.S. Thesis, Chulalongkorn University, Thailand, **1993**.
52. Billo, J. E. “Excel for Chemists: a comprehensive guide” 2nd ed., Wiley-VCH: New York, **2001**.



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APPENDIX A

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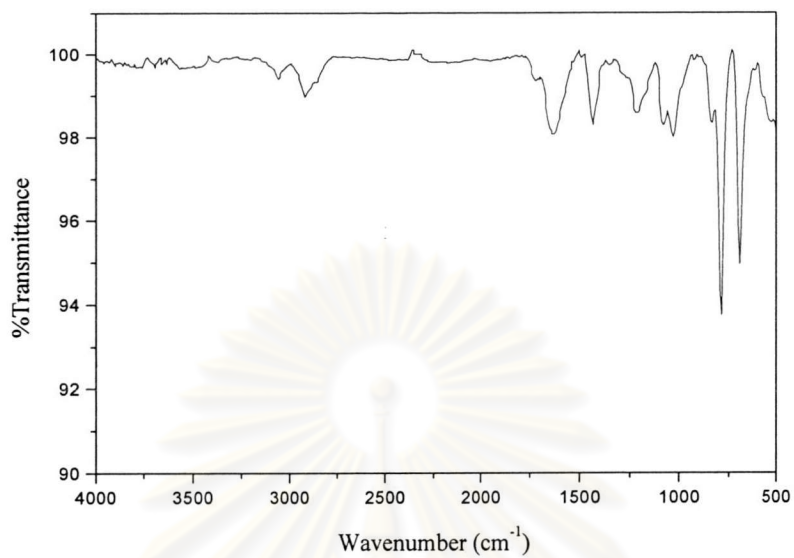


Figure A-1 FT-IR (KBr) spectrum of polythiophene

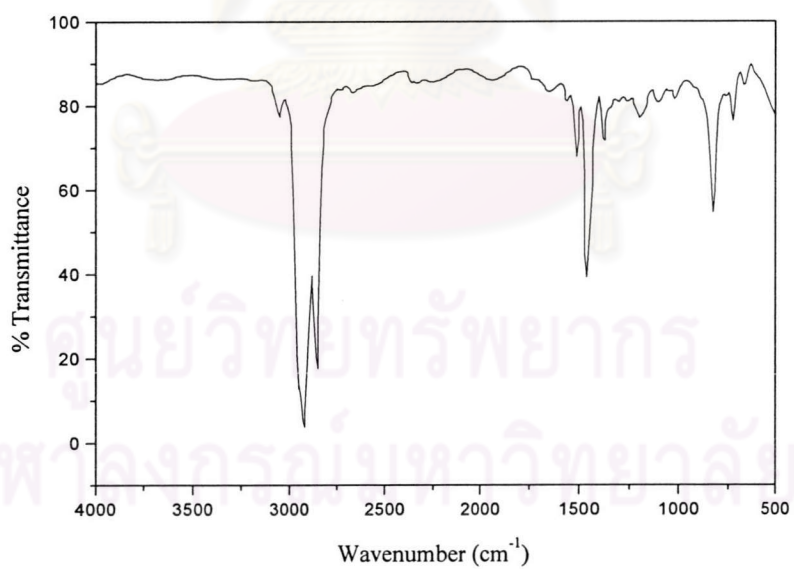


Figure A-2 FT-IR (film) spectrum of poly(3-hexylthiophene)

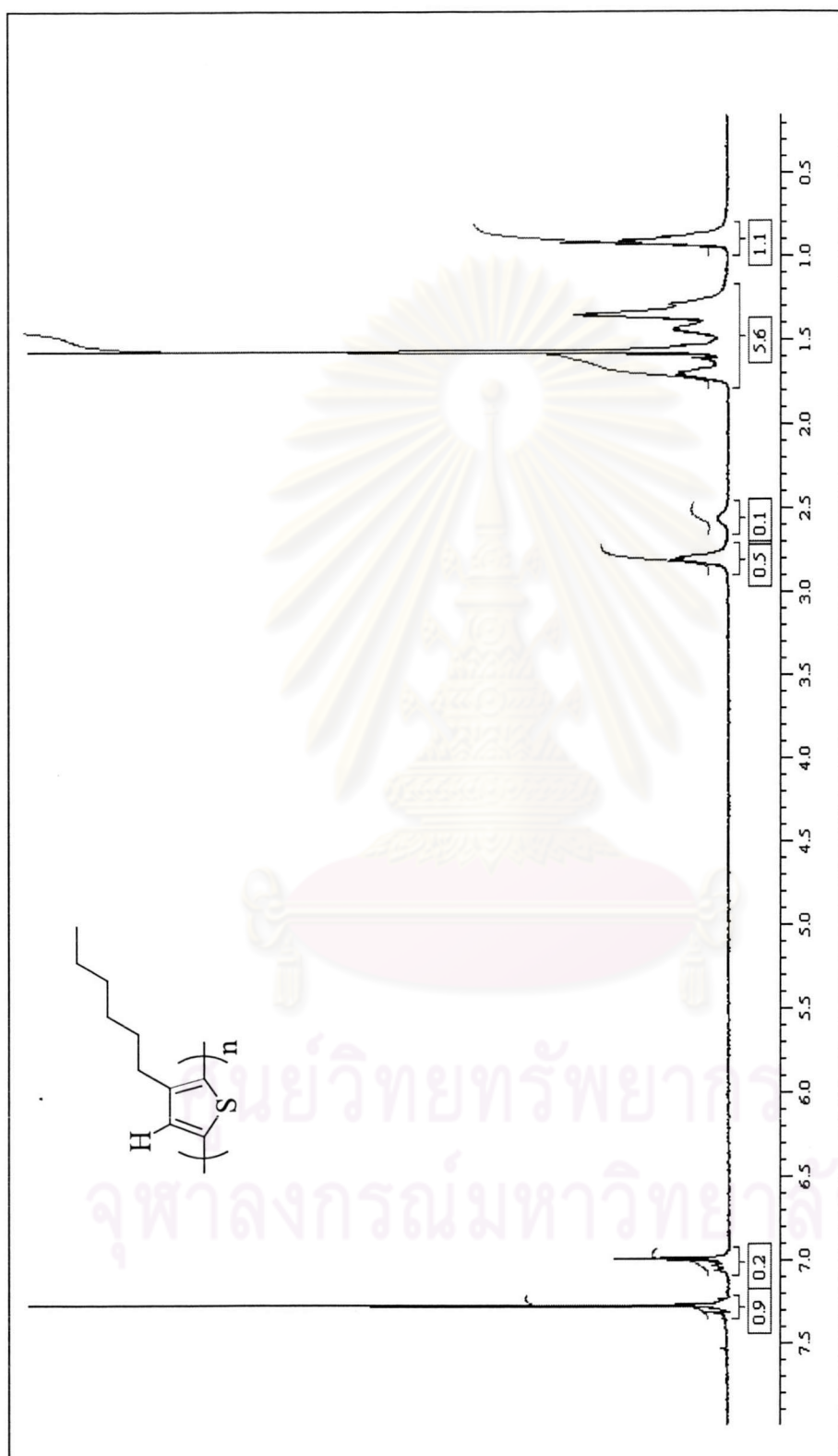


Figure A-3 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of poly(3-hexylthiophene)

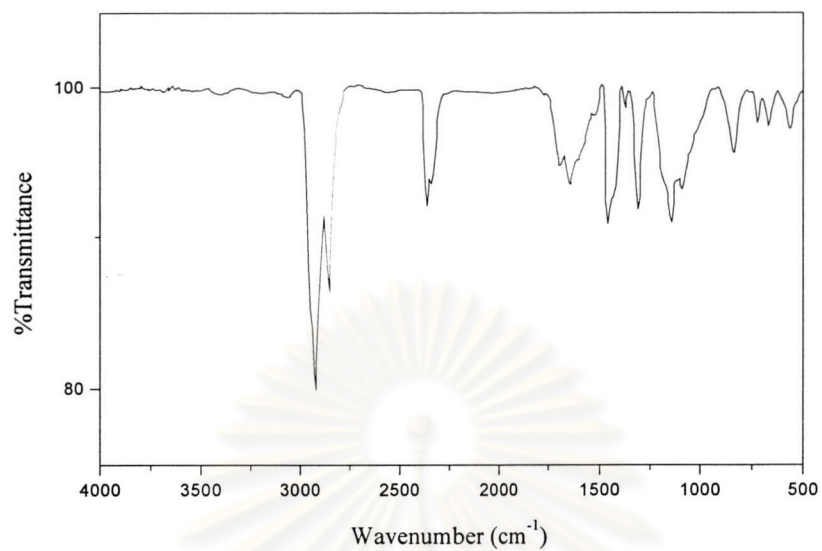


Figure A-4 FT-IR (KBr) spectrum of the oxidized poly(3-hexylthiophene)

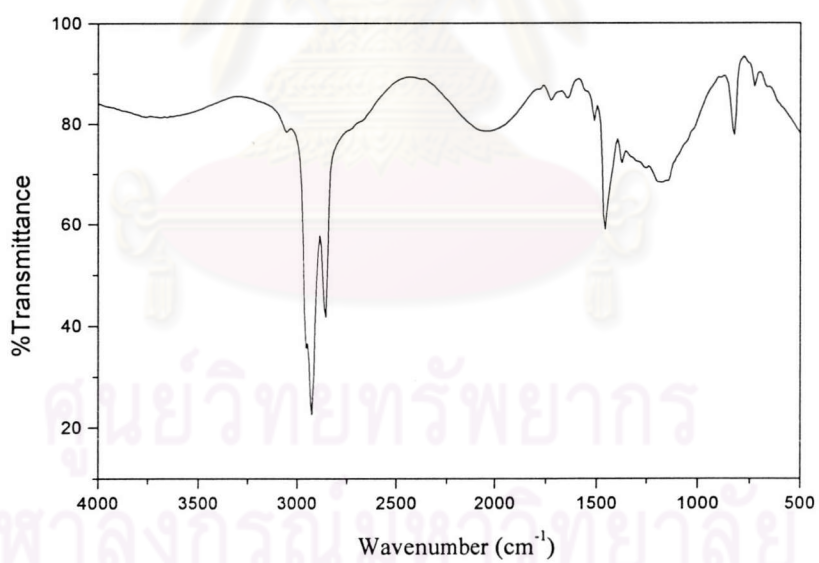


Figure A-5 FT-IR (film) spectrum of the oxidized poly(3-hexylthiophene)



APPENDIX B

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The Four-point Probe Method for Electrical Conductivity Measurement ⁵¹

Four tiny electrodes are arranged in straight line separated at exactly equal distances (d) and touched the surface of the sample to be measured. Then the electrodes are further connected with an electrical circuit equipped with an Amp meter (A) and a Voltmeter. (V) (**Figure B-1**) Contacts between the 4 electrodes and the sample surface must be equal. During the measurement, the current (I) is applied through electrode contact 1 to 4, and the potential difference (ΔV) across electrode contacts 2 and 3 is measured. The conductivity of the sample can be calculated from the equation **B-1**

$$\text{Conductivity (S.cm}^{-1}\text{); } \sigma = I/kVt \quad \dots\dots\dots (\text{B-1})$$

Where I is current (A)

k is probe constant

V is voltage (volt)

t is film thickness (cm)

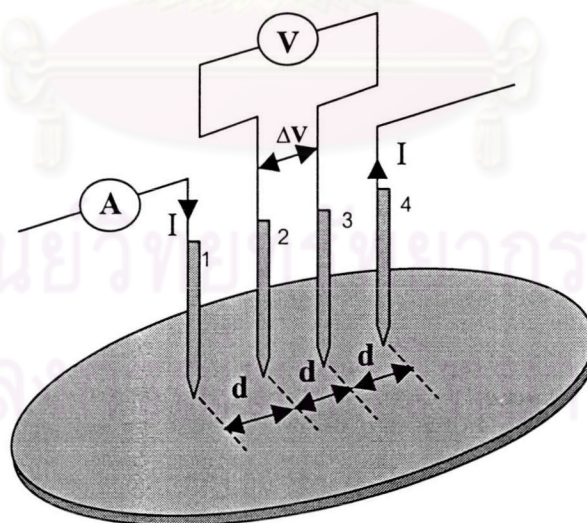


Figure B-1 Conductivity measurement by Four-point Probe method

The accuracy of the conductivity measurement by this method depends on:

i) the size of the sample, which must be very large compared to the separation distances (d) between the electrodes.

ii) thickness of the sample, which must be very small compared to the separation distances (d) between the electrodes.



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APPENDIX C

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Example of the calculation of AC-index

From UV-Visible spectroscopy data;

| a | b | x | f(x) | xf(x) |
|-------------------------|------------|-------------|----------------|---------------|
| λ (nm) | Absorbance | $(a1+a2)/2$ | $= (b1+b2)/2$ | |
| 310 | 0.208152 | 310.5 | 0.208563 | 64.75 |
| 311 | 0.208974 | 311.5 | 0.209521 | 65.26 |
| 312 | 0.210067 | 312.5 | 0.210774 | 65.86 |
| 313 | 0.21148 | 313.5 | 0.212073 | 66.48 |
| 314 | 0.212667 | 314.5 | 0.213511 | 67.14 |
| 315 | 0.214356 | 315.5 | 0.215014 | 67.83 |
| 316 | 0.215672 | 316.5 | 0.216622 | 68.56 |
| 317 | 0.217572 | 317.5 | 0.218448 | 69.35 |
| 318 | 0.219324 | 318.5 | 0.22029 | 70.16 |
| 319 | 0.221256 | 319.5 | 0.222245 | 71.00 |
| 320 | 0.223233 | - | - | - |
| Sum (310-320 nm) | | - | 2.14700 | 676.45 |

$$\text{AC-index}(310-320) = \frac{\sum xf(x)}{\sum f(x)} = \frac{676.4}{2.147} = 315.0$$

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APPENDIX D

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Table D-1 AC-index (310-700) and AC-index (310-900) of P3HT oxidized by *m*CPBA

| Entry | Reaction time (minute) | AC-index | |
|-------|---------------------------|------------|------------|
| | | 310-700 nm | 310-900 nm |
| 1 | 0 | 426.26 | 429.07 |
| 2 | 15 | 432.39 | 439.11 |
| 3 | 30 | 435.80 | 443.82 |
| 4 | 45 | 437.16 | 442.37 |
| 5 | 60 | 439.00 | 444.10 |

Table D-2 AC-index (310-700) and AC-index (310-900) of P3HT oxidized by H₂O₂/TFA (30 equivalence of TFA)

| Entry | Reaction time (minute) | AC-index | |
|-------|---------------------------|------------|------------|
| | | 310-700 nm | 310-900 nm |
| 1 | 0 | 431.46 | 424.72 |
| 2 | 30 | 433.69 | 428.30 |
| 3 | 60 | 436.76 | 431.85 |
| 4 | 90 | 436.70 | 433.25 |
| 5 | 120 | 443.11 | 435.13 |

Table D-3 AC-index (310-900) of P3HT oxidized by H₂O₂/TFA at 10 equivalence of TFA and 30 equivalence of TFA

| Entry | Reaction time (minute) | AC-index | |
|-------|---------------------------|--------------------|--------------------|
| | | 10 equivalence TFA | 30 equivalence TFA |
| 1 | 0 | 428.74 | 428.25 |
| 2 | 60 | 429.96 | 438.12 |
| 3 | 120 | 430.20 | 450.49 |
| 4 | 180 | 433.97 | 449.75 |
| 5 | 240 | 438.28 | 450.27 |

Table D-4 AC-index (300-1100) of P3HT solution doped by HClO₄; mole ratio P3HT: HClO₄ = 7 : 2

| Entry | Reaction time (minute) | AC-index (300-1100 nm) |
|-------|------------------------|------------------------|
| 1 | 0 | 427.3385 |
| 2 | 10 | 484.8086 |
| 3 | 20 | 521.0944 |
| 4 | 30 | 547.0144 |
| 5 | 40 | 562.5184 |
| 6 | 50 | 595.0704 |
| 7 | 60 | 600.3691 |
| 8 | 70 | 615.6876 |
| 9 | 80 | 631.0199 |
| 10 | 90 | 635.7626 |
| 11 | 100 | 649.7941 |
| 12 | 110 | 658.587 |
| 13 | 120 | 665.3054 |
| 14 | 130 | 667.5427 |

Table D-5 AC-index (300-1100) of P3HT solution doped by TFA; mole ratio P3HT: TFA = 6 : 5 and 3 : 5

| Entry | Reaction time (minute) | AC-index at mole ratio P3HT: TFA | |
|-------|------------------------|----------------------------------|----------|
| | | 6 : 5 | 3 : 5 |
| 1 | 0 | 428.0594 | 428.0594 |
| 2 | 10 | 463.5108 | 530.5357 |
| 3 | 20 | 484.3273 | 538.7685 |
| 4 | 30 | 485.4674 | 542.018 |
| 5 | 40 | 488.7551 | 543.4118 |

VITAE

Miss Krittiyapon Tepveera was born on February 28, 1976 in Pisanuloke, Thailand. She received a bachelor degree of science from Department of Chemistry, Faculty of Science, Chiangmai University, Thailand in 1998, and then worked at Winson Ink Co. Ltd. in the R&D position. In 2001, she was admitted to a Master's Degree Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed the program in 2004. Her address is 146/76 Premier place condominium 2, Suanluang, Bangkok, 10250.



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