



UNIVERSITY
OF WOLLONGONG
AUSTRALIA

University of Wollongong
Research Online

University of Wollongong Thesis Collection
1954-2016

University of Wollongong Thesis Collections

2005

Electrochemical and photovoltaic properties of poly(thiophene)s

George Tsekouras
University of Wollongong

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author.

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Recommended Citation

Tsekouras, George, Electrochemical and photovoltaic properties of poly(thiophene)s, PhD thesis, Department of Chemistry, University of Wollongong, 2005. <http://ro.uow.edu.au/theses/442>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

**ELECTROCHEMICAL AND PHOTOVOLTAIC
PROPERTIES OF POLY(THIOPHENE)S**

A thesis submitted in fulfilment of the
requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

GEORGE TSEKOURAS, BSc (Hons)

DEPARTMENT OF CHEMISTRY

October 2005

DECLARATION

This is to certify that the work described in this thesis is my own unless otherwise indicated and has not been submitted for qualifications at any other academic institution.

George Tsekouras

October 2005

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Prof Gordon Wallace and Dr Chee Too, for providing both general and technical advice, direction and support throughout the course of my study.

I greatly appreciate the help and support offered by all of my colleagues and friends at the Intelligent Polymer Research Institute (IPRI) at the University of Wollongong. In particular, I would like to acknowledge the technical assistance provided to me by Dr Jun Chen and Dr Peter Innis, and the administrative assistance given to me by Mr Elvis (Phil) Smugreski.

The efforts of Prof David Officer and his research group at the Nanomaterials Research Centre at Massey University, New Zealand, in the provision of polymer precursors and enlightening discussions, are greatly appreciated.

The financial support provided to me by the Australian Research Council (ARC) and by Prof Gordon Wallace for my PhD scholarship is greatly acknowledged.

Finally I dedicate this thesis to the memory of my late friend and colleague Dr Jeffrey (Gao) Jin, a man of great kindness and enthusiasm for life. The example you set is an inspiration to us all. I will remember you forever.

PUBLICATIONS

Tsekouras, G., Too, C.O. and Wallace, G.G., Effect of growth conditions on the photovoltaic efficiency of poly(terthiophene)-based photoelectrochemical cells, *Electrochimica Acta*, 50(16-17) (2005) 3224-3230.

CONFERENCE PRESENTATIONS

Tsekouras, G., Too, C.O. and Wallace, G.G., Conducting polymer solar cells (oral presentation), *26th Australasian Polymer Symposium (APS)*, Noosa, Australia, 2003.

Tsekouras, G., Too, C.O., Officer, D.L. and Wallace, G.G., Solar cells based on dye-doped poly(terthiophene) and a terthiophene derivative (oral presentation), *International Conference of Synthetic Metals (ICSM) Satellite Symposium*, Queenstown, New Zealand, 2004.

Tsekouras, G., Too, C.O. and Wallace, G.G., Morphology and photovoltaic characteristics of poly(terthiophene) (oral presentation), *International Conference of Synthetic Metals (ICSM)*, Wollongong, Australia, 2004.

Tsekouras, G., Too, C.O., Officer, D.L. and Wallace, G.G., Electrochemistry and photovoltaic characteristics of terthiophene and derivatives (oral presentation), *Interact*, Gold Coast, 2004.

Tsekouras, G., Too, C.O., Officer, D.L. and Wallace, G.G., Photovoltaic and electrochromic properties of poly(3-alkylthiophene)s and poly(4,4''-didecyloxyterthiophene)s (poster presentation), *2nd International Conference on Advanced Materials and Nanotechnology (AMN-2)*, Queenstown, New Zealand, 2005.

ABSTRACT

The utilisation of conducting polymers for photovoltaic applications represents the possibility of low-cost production of solar electricity. The chemical modification of the precursors used to prepare conducting polymers provides an avenue to the tuning of the photovoltaic, rheological and solubility properties of conducting polymers to suit photovoltaic applications.

Poly(thiophene)s have been widely utilised by researchers in the field of conducting polymer photovoltaics. The present study in part considered the utilisation of a range of thiophene precursors, in particular terthiophene derivatives, for the preparation of polymeric photoactive layers within photoelectrochemical cells. These precursors included a C₆₀-substituted terthiophene derivative, 3-alkylthiophenes and ether-substituted terthiophenes. Polymers synthesised from 3-alkylthiophene derivatives were also blended with a soluble C₆₀ derivative to give composite films. Terthiophene itself was used to prepare photoelectrochemical cells based on poly(terthiophene). The effects of the conditions used to electrochemically grow poly(terthiophene), such as solvent, electropolymerisation technique and electropolymerisation temperature, were investigated. In addition, the incorporation of commercially available anionic dyes and cationic dyes into poly(terthiophene) during electropolymerisation and post-growth electrochemical reduction, respectively, was considered.

The investigations made in this study may be classified according to one of the following strategies for improving the photovoltaic efficiency of photoelectrochemical cells based on poly(thiophene)s: controlling polymer morphology, enhancing light

absorption, improving exciton dissociation or increasing the efficiency of electron transfer at the interface between the photoactive layer and liquid electrolyte. In this way the investigations in this study were all targeted at improving a particular aspect of the photovoltaic effect in photoelectrochemical cells.

In addition to the characterisation of the photovoltaic properties of the photoactive materials prepared, such materials were also characterised using techniques that included post-growth cyclic voltammetry, UV-Vis spectroscopy, photocurrent action spectroscopy, scanning electron microscopy and *in situ* spectroelectrochemistry. The results obtained from such characterisations gave an insight into the photovoltaic properties observed, in addition to general information on the properties of the photoactive materials investigated.

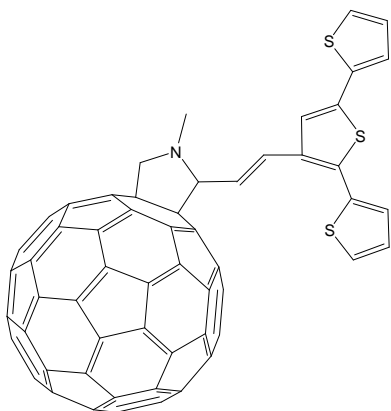
ABBREVIATIONS

| | |
|-----------------------|---|
| A | Area |
| A ⁻ | Anion |
| ACN | Acetonitrile |
| AFM | Atomic Force Microscopy |
| C ⁺ | Cation |
| CE | Constant Potential |
| CI | Constant Current |
| CN-PPV | Cyano-substituted poly(<i>p</i> -phenylene vinylene) |
| CP | Conducting Polymer |
| CV | Cyclic Voltammetry |
| CrV | Crystal Violet |
| DCM | Dichloromethane |
| EC | Ethylene Carbonate |
| E _{onset.ox} | Potential at the Onset of Oxidation |
| EtOH | Ethanol |
| EV | Ethyl Violet |
| FF | Fill Factor |
| HH | Head-to-Head |
| ¹ H NMR | Proton Nuclear Magnetic Resonance |
| HT | Head-to-Tail |
| I _l | Illumination Intensity |
| I _{pp} | Current-at-Peak-Power |
| I _{sc} | Short-Circuit-Current |

| | |
|----------|--|
| ITO | Indium Tin Oxide |
| I-V | Current-Voltage |
| LESR | Light-induced Electron Spin Resonance |
| LSV | Linear Sweep Voltammetry |
| MDMO-PPV | Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)- <i>p</i> -phenylene vinylene] |
| MEH-PPV | Poly(2-methoxy-5-(2'-ethylhexyloxy)- <i>p</i> -phenylene vinylene) |
| MeOH | Methanol |
| M_n | Number-averaged Molecular Weight |
| M_w | Weight-averaged Molecular Weight |
| NBB | Naphthol Blue Black |
| PA | Poly(acetylene) |
| PAn | Poly(aniline) |
| P(3AT) | Poly(3-alkylthiophene) |
| P(BTh) | Poly(2,2'-bithiophene) |
| PB-VF | Patent Blue VF |
| PC | Propylene Carbonate |
| PCBM | [6,6]-phenyl C ₆₁ -butyric acid methyl ester |
| PCE | Power Conversion Efficiency |
| P(3DDT) | Poly(3-dodecylthiophene) |
| PDI | Polydispersity Index |
| PEC | Photoelectrochemical Cell |
| PEO | Polyethylene Oxide |
| PET | Poly(ethylene terephthalate) |
| P(3HT) | Poly(3-hexylthiophene) |
| PL | Photoluminescence |

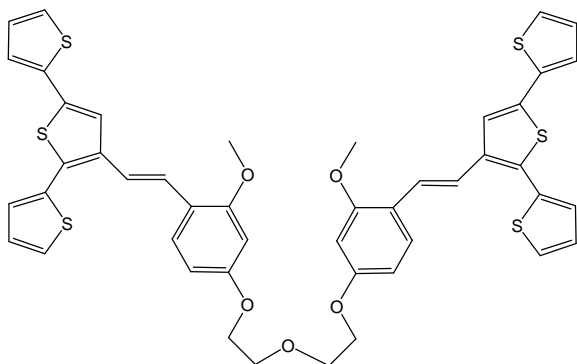
| | |
|-----------------|--|
| P(3MT) | Poly(3-methylthiophene) |
| P(3OT) | Poly(3-octylthiophene) |
| PPV | Poly(<i>p</i> -phenylene vinylene) |
| PPy | Poly(pyrrole) |
| PS | Polystyrene |
| PTh | Poly(thiophene) |
| P(TTh) | Poly(2,2':5',2''-terthiophene) |
| Q | Charge |
| S-B | Sulforhodamine B |
| SEC | Size Exclusion Chromatography |
| SEM | Scanning Electron Microscopy |
| TBAP | Tetrabutylammonium Perchlorate |
| TEM | Tunnelling Electron Microscopy |
| THF | Tetrahydrofuran |
| TPAI | Tetrapropylammonium Iodide |
| TPP-Th | 3-tetraphenylporphyrinthiophene |
| TPP-TTh | 3'-tetraphenylporphyrin-2,2':5',2''-terthiophene |
| UV-Vis | Ultra Violet-Visible |
| VB-R | Victoria Blue R |
| V_{oc} | Open-Circuit-Voltage |
| VPB-BO | Victoria Pure Blue BO |
| V_{pp} | Voltage-at-Peak-Power |
| XC-FF | Xylene Cyanole FF |
| λ_{max} | Wavelength of Maximum Absorption |

MONOMER SYMBOLS



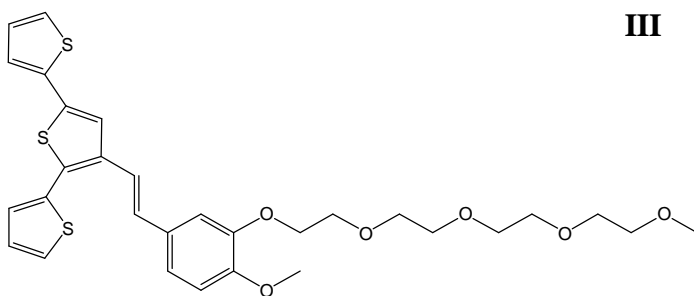
I

N-Methyl-2-(2-[2,2';5',2''-
terthiophen-3'-
yl]ethenyl)fullero[3,4]pyrrolidine



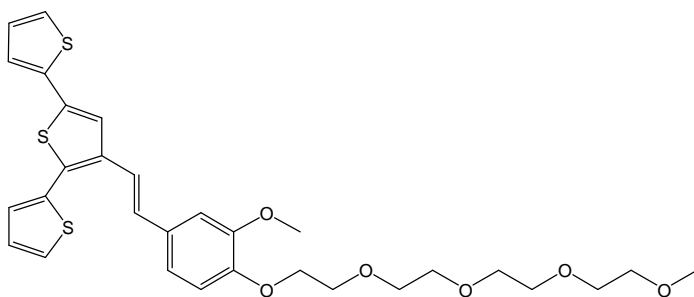
II

1,7-bis[3-methoxy-4-(2-
[2,2':5',2''-terthiophen-3'-
yl]ethenyl)phenyl]-1,4,7-
trioxahexane



III

3'-(2-[4-methoxy-3-(3,6,9,12-
tetraoxatridec-1-
yloxy)phenyl]ethenyl)-
2,2':5',2''-terthiophene



IV

3'-(2-[3-methoxy-4-(3,6,9,12-
tetraoxatridec-1-
yloxy)phenyl]ethenyl)-
2,2':5',2''-terthiophene

CONTENTS

| | |
|-------------------------------|-----|
| Declaration | I |
| Acknowledgements | II |
| Publications | III |
| Abstract | V |
| Abbreviations | VII |
| Monomer Symbols | X |

CHAPTER 1:

| | |
|--|----|
| GENERAL INTRODUCTION | 1 |
| 1.1 The Case for Photovoltaics | 2 |
| <i>1.1.1 The Energy Crisis</i> | 2 |
| <i>1.1.2 Renewable Energy</i> | 3 |
| <i>1.1.3 Current Photovoltaic Energy Systems</i> | 6 |
| 1.2 Introduction to Conducting Polymers | 8 |
| 1.3 The Photovoltaic Effect in Conducting Polymers | 13 |
| 1.4 Conducting Polymer Solar Cell Configurations | 16 |
| 1.5 Progress in Conducting Polymer Photovoltaics | 18 |
| <i>1.5.1 Utilisation of Poly(p-phenylene vinylene)s in Photovoltaics</i> | 19 |
| <i>1.5.2 Utilisation of Poly(thiophene)s in Photovoltaics</i> | 26 |
| 1.6 Aims of Study | 41 |
| 1.7 References | 43 |

CHAPTER 2:

| | |
|--|----|
| GENERAL EXPERIMENTAL | 50 |
| 2.1. Reagents and Materials | 51 |
| 2.2. Instrumentation | 51 |
| 2.3. Electropolymerisation | 52 |
| 2.4. Post-Growth Electrochemical Characterisation | 54 |
| 2.5 UV-Vis Spectroscopy | 54 |
| 2.6 Photoelectrochemical Cell Fabrication | 54 |
| 2.7 Photovoltaic Testing | 56 |
| 2.8 Photocurrent Action Spectroscopy | 57 |
| 2.9 Spectroelectrochemical Characterisation | 57 |

CHAPTER 3:

EFFECT OF GROWTH CONDITIONS ON THE PHOTOVOLTAIC EFFICIENCY OF POLY(TERTHIOPHENE)-BASED

| | |
|---|----|
| PHOTOELECTROCHEMICAL CELLS | 60 |
| 3.1 Introduction | 61 |
| 3.2 Experimental | 61 |
| 3.3 Results and Discussion | 64 |
| 3.3.1 <i>General Electrochemical and Photoelectrochemical Properties of Poly(terthiophene)</i> | 64 |
| 3.3.2 <i>Effect of Solvent used for Growth of Poly(terthiophene)</i> | 68 |
| 3.3.3 <i>Effect of Electrochemical Technique used for Polymer Growth</i> | 71 |

| | | |
|-------|--|----|
| 3.3.4 | <i>Effect of the Upper Potential Limit used for Growth By Cyclic Voltammetry</i> | 73 |
| 3.3.5 | <i>Effect of Electropolymerisation Temperature</i> | 78 |
| 3.3.6 | <i>Combining Optimum Conditions for the Electrochemical Growth of Poly(terthiophene)</i> | 85 |
| 3.4 | Conclusions | 87 |
| 3.5 | References | 89 |

CHAPTER 4:

PHOTOVOLTAIC PROPERTIES OF POLY(TERTHIOPHENE)

| | |
|--|-----|
| DOPED WITH DYES | 90 |
| 4.1 Introduction | 91 |
| 4.2 Experimental | 94 |
| 4.3 Results and Discussion | 96 |
| 4.3.1 <i>Growth and Characterisation of Poly(terthiophene) doped with Sulforhodamine B</i> | 96 |
| 4.3.2 <i>Growth and Characterisation of Poly(terthiophene) doped with Patent Blue VF</i> | 103 |
| 4.3.3 <i>Growth and Characterisation of Poly(terthiophene) doped with Naphthol Blue Black</i> | 109 |
| 4.3.4 <i>Attempted Growth of Poly(terthiophene) doped with Xylene Cyanole FF</i> | 116 |
| 4.3.5 <i>Growth and Characterisation of Poly(terthiophene) doped with mixture of Sulforhodamine B and Patent Blue VF</i> | 116 |

| | | |
|-------|---|-----|
| 4.3.6 | <i>Investigations into the Incorporation of Cationic Dyes into Poly(terthiophene) doped with Sulforhodamine B</i> | 120 |
| 4.4 | Conclusions | 123 |
| 4.5 | References | 125 |

CHAPTER 5:

ELECTROCHEMISTRY OF A C₆₀-SUBSTITUTED TERTHIOPHENE AND CHARACTERISATION OF

| | | |
|-------|--|-----|
| | POLYMERS AND COPOLYMERS | 127 |
| 5.1 | Introduction | 128 |
| 5.2 | Experimental | 129 |
| 5.3 | Results and Discussion | 130 |
| 5.3.1 | <i>Growth and Characterisation of P(I) Homopolymer</i> | 130 |
| 5.3.2 | <i>Growth and Characterisation of Polymers Containing I and TTh</i> | 134 |
| 5.3.3 | <i>Effect of I:TTh Ratio on the Properties of Polymers Containing I and TTh</i> | 139 |
| 5.3.4 | <i>Spectroelectrochemistry of P(I), Polymer Containing I and TTh, and P(TTh)</i> | 145 |
| 5.4 | Conclusions | 149 |
| 5.5 | References | 150 |

CHAPTER 6:

SYNTHESIS OF SOLUBLE POLY(3-ALKYLTHIOPHENE)S

AND USE AS PHOTOVOLTAIC AND

| | |
|--|-----|
| ELECTROCHROMIC MATERIALS | 151 |
| 6.1 Introduction | 152 |
| 6.2 Experimental | 153 |
| 6.2.1 Reagents and Materials | 153 |
| 6.2.2 Instrumentation | 154 |
| 6.2.3 Oxidative Polymerisation of 3-alkylthiophenes | 154 |
| 6.2.4 Spin Casting and Characterisation of Poly(3-alkylthiophene) and Poly(3-alkylthiophene)/PCBM Films | 155 |
| 6.2.5 Electropolymerisation of 3-alkylthiophenes and Characterisation of Resultant Polymers | 156 |
| 6.3 Results and Discussion | 156 |
| 6.3.1 Characterisation of Poly(3-alkylthiophene)s by Size Exclusion Chromatography and Proton Nuclear Magnetic Resonance Spectroscopy | 156 |
| 6.3.2 Properties of Poly(3-hexylthiophene) Films | 162 |
| 6.3.3 Properties of Poly(3-octylthiophene) Films | 169 |
| 6.3.4 Properties of Poly(3-hexylthiophene)/PCBM Films | 176 |
| 6.3.5 Properties of Poly(3-octylthiophene)/PCBM Films | 182 |
| 6.3.6 Investigations into the Electropolymerisation of 3-alkylthiophenes and Characterisation of Resultant Polymers | 186 |

| | | | |
|---|---|-------|-----|
| 6.4 | Conclusions | | 192 |
| 6.5 | References | | 195 |
| | | | |
| CHAPTER 7: | | | |
| ELECTROCHEMISTRY OF ETHER-SUBSTITUTED | | | |
| TERTHIOPHENES AND PHOTOVOLTAIC PROPERTIES | | | |
| OF POLYMERS AND COPOLYMERS | | | |
| | | | 196 |
| 7.1 | Introduction | | 197 |
| 7.2 | Experimental | | 199 |
| 7.3 | Results and Discussion..... | | 200 |
| 7.3.1 | <i>Electrodeposition and Characterisation of P(II)</i> | | 200 |
| 7.3.2 | <i>Electrodeposition and Characterisation of</i> | | |
| | <i>Polymer containing II and Terthiophene</i> | | 205 |
| 7.3.3 | <i>Electrodeposition and Characterisation of P(III)</i> | | 211 |
| 7.3.4 | <i>Electrodeposition and Characterisation of</i> | | |
| | <i>Polymer containing III and Terthiophene</i> | | 214 |
| 7.3.5 | <i>Electrodeposition and Characterisation of P(IV)</i> | | 220 |
| 7.3.6 | <i>Electrodeposition and Characterisation of</i> | | |
| | <i>Polymer containing IV and Terthiophene</i> | | 224 |
| 7.4 | Conclusions | | 230 |
| 7.5 | References | | 231 |
| | | | |
| GENERAL CONCLUSIONS | | | 233 |
| | | | |
| APPENDIX A: TABLE OF PHOTOVOLTAIC PROPERTIES FOR | | | |
| BEST PHOTOELECTROCHEMICAL CELLS | | | 237 |