

Denis Fichou

Handbook of Oligo- and Polythiophenes

 **WILEY-VCH**

Weinheim · New York · Chichester · Brisbane · Singapore · Toronto

This Page Intentionally Left Blank

Denis Fichou

Handbook of Oligo- and Polythiophenes

 **WILEY-VCH**

Related titles from WILEY-VCH

K. Müllen / G. Wegner

Electronic Materials: The Oligomer Approach

ISBN 3-527-29438-4, WILEY-VCH 1998.

S. Roth

One-Dimensional Metals

ISBN 3-527-26875-8, WILEY-VCH 1995.

Denis Fichou

Handbook of Oligo- and Polythiophenes

 **WILEY-VCH**

Weinheim · New York · Chichester · Brisbane · Singapore · Toronto

Dr. Denis Fichou
Laboratoire des Matériaux Moléculaires
C.N.R.S.
2, rue Henry-Dunant
F-94320 Thiais
France

This book was carefully produced. Nevertheless, authors, editor and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloguing-in-Publication Data:

Fichou, Denis:

Handbook of oligo- and polythiophenes / Denis Fichou. – Weinheim ;
New York ; Chichester ; Brisbane ; Singapore ; Toronto : Wiley-VCH, 1999
ISBN 3-527-29445-7

© WILEY-VCH Verlag GmbH, D-69469 Weinheim (Federal Republic of Germany), 1999

Printed on acid-free and chlorine-free paper

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition: Alden Bookset, Oxford, England

Printing: betzdruck, D-64291 Darmstadt

Bookbinding: Großbuchbinderei J. Schäffer, D-67269 Grünstadt

Printed in the Federal Republic of Germany

Preface

At the eve of the 21st century and after twenty years of maturation, the world of conjugated polymers and oligomers is a flourishing branch of materials science with many opportunities for applications in electronics and photonics. Polyaniline, poly(*p*-phenylenevinylene) and polythiophene are among the most investigated conjugated polymers that combine the electronic and optical properties of semiconductors with the processing advantages and mechanical plasticity of conventional polymers. Depending upon their doping level, these versatile materials behave either as metallic conductors or semiconductors, can be chromophores or lumino-phores and may even develop large optical nonlinearities. When doped to metallic levels, conjugated polymers become highly conducting and may find applications in batteries, electrochromic or smart windows, electromagnetic shields, antistatic coatings and various types of sensors. On the other hand, when in the semiconducting form they exhibit similar electrical and optical properties as inorganic semiconductors. High performance optoelectronic devices fabricated from conjugated polymers such as light emitting diodes, field-effect transistors, photodetectors, photovoltaic cells, optocouplers and light modulators have been demonstrated. Although most of these polymer products still face technical problems and are not yet commercialized, they preconceive what could be in a near future the world of “plastic electronics”.

Oligo- and polythiophenes (PT) present all aspects of a rich and homogeneous family of conjugated compounds, thanks to the extraordinary fecundity of thiophene chemistry. Since the discovery of conducting PT in 1982 at CNRS in Thiais, France, a tremendous number of substituted derivatives have been synthesized and their electronic properties investigated. If one of the early goals has been to improve the conductivity by controlling the growth and structure of the polymer, very rapidly new targets emerged.

Grafting an adequate substituent on the main PT chain on a lateral carbon site provides an additional property such as solubility which is required to prepare free-standing films on any surface. Other substituents allow to introduce optical, magnetic or liquid crystalline properties. Beside, “functionalized” PTs combine electrical conductivity together with a second activity that can be triggered by electricity. Depending on this functionalization, PT derivatives can operate complex functions like for example selective recognition of biomolecules (DNA, oligonucleotides).

Another important research field aims at controlling the molecular and structural ordering of semiconducting PT in view of improving its charge transport properties. A major advance in this direction has been realized in 1987 at CNRS, Thiais, with the synthesis of sexithiophene (6T), the linear hexamer of thiophene, and its use to fabricate an organic transistor whose performances are close to those of silicon-based devices. The spectacular increase of the carrier mobility in polycrystalline

6T films as compare to disordered PT is the result of three criteria generally met by low-molecular weight oligomers:

1. high molecular order (defect-free molecules),
2. high chemical purity (up to electronic grade) and
3. high structural order in the solid state (up to single crystals).

The concept of well-defined oligomers was born and rapidly extended to other compounds (arylenevinylenes, polyenes, acenes, etc. . . .) to turn into one of the most successful routes in the modern world of conjugated organics.

This Handbook summarizes in ten chapters all aspects of oligo- and polythiophenes as they developed over the last twenty years, from chemistry to physics and applications. It has been written by the most reknown experts in the field worldwide, from both academics and industrial origins, with a constant care of clarity through concise texts and an extensive use of figures and tables. This first review on PTs and oligomers constitutes a comprehensive tool not only for researchers but also for advanced students and anyone willing to get informations on this novel class of materials.

Denis Fichou
October 1998

Contents

1	The Chemistry of Conducting Polythiophenes: from Synthesis to Self-Assembly to Intelligent Materials	1
	<i>Richard D. McCullough</i>	
1.1	Introduction	1
1.2	Chemical Synthesis of Unsubstituted Polythiophene (PT)	2
1.3	Chemical Synthesis of Polyalkylthiophenes (PATs)	5
1.3.1	Straight Alkyl Side Chains	5
1.3.1.1	Chemical Synthesis of PATs	5
1.3.1.1.1	Metal Catalyzed Cross-coupling Polymerizations	5
1.3.1.1.2	FeCl ₃ Method for the Polymerization of PATs	6
1.3.1.2	Comparison of the Above Methods	8
1.3.1.3	Regioregular PATs	9
1.3.1.3.1	Regioregular HH-TT and TT-HH PATs	10
1.3.1.4	Regioregular, Head-to-Tail Coupled PATs	12
1.3.1.4.1	The McCullough Method	12
1.3.1.4.2	The Rieke Method	13
1.3.1.4.3	The Mechanism and Catalyst Choice	15
1.3.1.4.4	NMR Characterization of HT-PAT	15
1.3.1.4.5	IR and UV-Vis	16
1.3.1.4.6	Self-Assembly, X-ray, and Electrical Conductivity in HT-PATs	18
1.3.1.4.7	Other Methods	19
1.3.1.4.8	Random Copolymers of Alkyl Thiophenes	20
1.3.1.4.9	Head-to-Tail Coupled, Random Copolymers of Alkyl Thiophenes	20
1.3.1.5	Branched Alkyl PATs	21
1.3.1.6	PTs with Phenyl Sidechains	24
1.4	Chemical Synthesis of Heteroatomic Functionalized Substituents on PTs: Recognition Sites for Self-Assembly and Chemical Sensing	24
1.4.1	Chemical Synthesis of Alkoxy Polythiophenes	25
1.4.2	Chemically Prepared Alkoxy PTs as Conducting Polymer Sensors	27
1.4.3	Chiral Substituents on PT	32
1.4.4	Carboxylic Acid Derivatives: Self-Assembly and Sensors	33
1.4.5	Other Derivatives of PT	34
1.5	Fused Rings Systems	38
1.6	Conclusion	39
	References	39

2	Electronic Properties of Polythiophenes	45
	<i>Shu Hotta and Kohzo Ito</i>	
2.1	General Aspects of Conducting Polymers	45
2.2	Structure and Conformation of Polythiophenes	48
2.2.1	Morphology and Crystal Structure	48
2.2.2	Conformational Features	52
2.3	Electronic Processes of Polythiophenes	57
2.3.1	Charge Excitations in Polythiophenes	57
2.3.2	Charge Transport in Polythiophenes	60
2.3.3	Carrier Recombination: Photoluminescence and Electroluminescence	63
2.3.4	Spectroscopic Studies of the Charged States	65
2.3.4.1	Charge Storage Configurations in Solids and their Anisotropic Properties	65
2.3.4.2	Properties in Solutions	73
2.4	Concluding Remarks and Future Outlook	80
	Acknowledgments	82
	References	82
3	The Synthesis of Oligothiophenes	89
	<i>Peter Bäuerle</i>	
3.1	Introduction	89
3.2	Synthesis of Oligothiophenes	93
3.2.1	Unsubstituted Oligothiophenes	93
3.2.1.1	Arene/arene-Coupling Methods by Oxidative Couplings	93
3.2.1.2	Transition Metal Catalyzed Coupling Methods	97
3.2.1.3	Ring Closure Reactions from Acyclic Precursors	104
3.2.1.4	Physical Properties of α -oligothiophenes and Isomers	111
3.2.2	Substituted Oligothiophenes	118
3.2.2.1	β, β' -Substituted Oligothiophenes	119
3.2.2.2	α, α' -Substituted Oligothiophenes	139
3.2.2.3	α, β -Substituted Oligothiophenes	145
3.2.2.4	Functionalized Oligothiophenes	155
3.2.2.5	Amphiphilic Oligothiophenes	170
3.2.2.6	Transition Metal Complexes of Oligothiophenes	171
3.3	Conclusion	172
	Acknowledgement	173
	References	173
4	Structure and Properties of Oligothiophenes in the Solid State: Single Crystals and Thin Films	183
	<i>Denis Fichou and Christiane Ziegler</i>	
4.1	Introduction	183
4.2	Single Crystals	184

4.2.1	General Description	184
4.2.2	X-ray Structures	187
4.2.2.1	Bithiophene (α -2T) and Derivatives	187
4.2.2.2	α -Terthiophene (α -3T) and Derivatives	191
4.2.2.3	α -Quaterthiophene (α -4T) and Derivatives	193
4.2.2.4	α -Quinquethiophene (α -5T) and Derivatives	202
4.2.2.5	α -Sexithiophene (α -6T) and Derivatives	203
4.2.2.6	α -Octithiophene (α -8T)	207
4.2.2.7	Polythiophene and 3-Alkylated Derivatives	213
4.2.3	Optical and Electrical Properties	214
4.2.3.1	General Remarks	214
4.2.3.2	Dimethylquarterthiophene	214
4.2.3.3	α -Sexithiophene (α -6T)	215
4.2.3.4	α -Octithiophene (α -8T)	216
4.3	Thin films	220
4.3.1	Deposition Techniques	220
4.3.1.1	Vacuum deposition Techniques	220
4.3.1.2	Preparation from Solution	220
4.3.2	Morphology	221
4.3.2.1	General Remarks	221
4.3.2.2	Monothiophene (IT) and Derivatives	222
4.3.2.3	Small Oligomers (α -2T– α -4T) and Derivatives	223
4.3.2.4	Quinquethiophene (α -5T) and Derivatives	226
4.3.2.5	Sexithiophene (α -6T) and Derivatives	234
4.3.2.6	Longer Obligothiophenes (α -7T, α -8T) and Derivatives	244
4.3.2.7	Polythiophene and Derivatives	245
4.3.3	Optical Characterization	247
4.3.3.1	Undoped Oligothiophenes	247
4.3.3.2	Charges in Oligothiophenes	257
4.3.4	Electrical Characterization	266
4.3.4.1	General Remarks	266
4.3.4.2	Contacts, I/V-Curves, Carrier Injection	267
4.3.4.3	Influence of the Structure on Conductivity Data	269
4.3.4.4	Influence of the Structure on Mobility Data	270
4.3.4.5	Temperature Dependence	271
4.3.4.6	Conjugation Length Influence	272
4.3.4.7	Influence of Dopants	272
4.3.4.8	Photoconductivity	274
	References	274

5 Charge Transport in Semiconducting Oligothiophenes 283

Gilles Horowitz and Phillippe Delannoy

5.1	Basic Models	284
5.1.1	The Band Model	284

5.1.2	Hopping	288
5.1.2.1	Localization	288
5.1.2.2	Temperature Dependence	289
5.1.2.3	Field Dependent Mobility	291
5.1.3	Polarons	291
5.1.3.1	Small Polaron	291
5.1.3.2	Molecular ‘Nearly Small’ Polaron	293
5.1.3.3	Polarons in π -Conjugated Polymers and Oligomers	295
5.1.4	Multiple Trapping	297
5.1.5	Summary	297
5.2	Measurement of the Mobility	298
5.2.1	Conductivity	298
5.2.2	Time of Flight	299
5.2.3	Space-Charge-Limited Current	300
5.2.3.1	Profile of Injected Charges	301
5.2.3.2	Estimation of the Space-Charge Limited Current	302
5.2.3.3	Effect of Traps	303
5.2.4	Field-Effect	305
5.3	Transport properties of Oligothiophenes	306
5.3.1	Conductivity, Mobility and Carrier Density	307
5.3.1.1	Variation with Chain Length	307
5.3.1.2	Carrier Density	308
5.3.1.3	Variation with Temperature	309
5.3.2	Traps	311
5.4	Concluding Remarks	312
	References	313

6 **Geometric and Electronic Structure and Optical Response of Oligo- and Polythiophenes: Relation to Their Use in Electro-optic and Photonic Devices** 317

J. Cornil, D. Beljonne, V. Parente, R. Lazzaroni, and J. L. Brédas

6.1	Introduction	317
6.2	Theoretical Methodology	320
6.3	Electronic and Linear Optical properties of Neutral Oligothiophenes	322
6.3.1	Nature of the Lowest Excited States	322
6.3.2	Intersystem Crossing Processes	324
6.3.3	Lattice Relaxation Phenomena	326
6.3.4	Effects of Substitution	328
6.4	Electronic and Linear Optical Properties of Charged Oligothiophenes	333
6.5	Characterization of Metal/polymer Interfaces	339
6.5.1	Geometric Structures	340
6.5.2	Electronic Structures	343

6.5.3	Vibrational Signature	344
6.6	Nonlinear Optical Properties of Neutral Oligothiophenes	347
6.6.1	Chain Length Dependence of the third-order Polarizabilities in Thiophene Oligomers	349
6.6.2	Dynamic Third-order Response of Th7: Two-photon Absorption and Third-harmonic Generation	352
6.7	Synopsis	355
	Acknowledgements	355
	References	357

7 **Electronic Excited States of Conjugated Oligothiophenes** 361

Carlo Taliani and Wolfram Gebauer

7.1	Introduction	361
7.2	Electronic Structure of Conjugated Polymers	362
7.2.1	General Concept	362
7.2.2	Polythiophene	363
7.3	Oligothiophene Model Structure	364
7.3.1	Molecular Structure	364
7.3.2	Singlet States	367
7.3.2.1	Assignments	367
7.3.2.2	Chain Length Dependence	368
7.3.2.3	Nature of the Lowest Singlet Transition	369
7.3.2.4	Franck–Condon Coupling	370
7.3.3	Triplet States	372
7.4	Solid State Properties	373
7.4.1	Molecular Packing	373
7.4.2	Theoretical Approach	374
7.4.2.1	The Exciton Concept and the Lowest Excited State in 6T	374
7.4.2.2	Higher Transitions – Extended States	379
7.4.3	Experimental Evidence for the Nature of the Lowest Excited States	380
7.4.3.1	Structural and Morphological Aspects of Polycrystalline Thin Films	380
7.4.3.2	Optical Properties of Thin Polycrystalline Films	384
7.4.3.3	Highly Ordered Systems	387
7.4.3.4	Two-photon Excitation	392
7.4.3.5	Extended States	392
7.4.3.6	Triplet States	393
7.4.3.7	Excited States Ordering	394
7.5	Polarized Electroluminescence	395
7.6	Nonlinear Optical Properties of Polythiophene and Thiophene Oligomers	397
	Acknowledgements	400
	References	400

8 Electro-optical Polythiophene Devices 405*Magnus Granström, Mark G. Harrison, and Richard H. Friend*

- 8.1 Overview 405
 - 8.1.1 Relationship Between Polymers and Oligomers 405
- 8.2 Preparation of Thin Film Devices 408
 - 8.2.1 Introduction 408
 - 8.2.2 Polymers 408
 - 8.2.3 Oligomers 409
 - 8.2.4 Relative Merits of the Different Methods to Achieve Solubility 410
 - 8.2.4.1 Substitution with Side-chains 410
 - 8.2.4.2 Using a Soluble Partially-conjugated Precursor Polymer 412
 - 8.2.5 Blends Between Polymer and Oligomers 413
- 8.3 Electronic Excitations in Oligothiophenes 413
 - 8.3.1 Introduction 413
 - 8.3.2 Intra-molecular Non-radiative Decay Channels 413
 - 8.3.2.1 Internal Conversion 415
 - 8.3.2.2 Intersystem Crossing 416
 - 8.3.2.3 Singlet Fission 417
 - 8.3.3 Inter-molecular Non-radiative Decay Channels in Thin Films 417
 - 8.3.3.1 Aggregation and Davydov Splitting 417
 - 8.3.3.2 Charge-transfer Excitons 418
 - 8.3.4 Effects of Inter-ring Torsion and Coplanarity of Oligomers 419
 - 8.3.4.1 Solution 420
 - 8.3.4.2 Solid State 420
 - 8.3.5 Concluding Remarks 421
- 8.4 Electroluminescent Devices 421
 - 8.4.1 Introduction 421
 - 8.4.2 Historical Survey of Organic LEDs 424
 - 8.4.2.1 LEDs Based on Molecular Semiconductors 424
 - 8.4.2.2 Polymeric LEDs 425
 - 8.4.3 LEDs Based on Oligothiophenes 427
 - 8.4.4 LEDs Based on Polythiophenes 429
 - 8.4.4.1 Polythiophene LEDs Covering the Whole Visible Spectrum and a Bit More 430
 - 8.4.4.2 Intrinsically-polarised Polymer LEDs 432
 - 8.4.4.3 Polythiophenes in Microcavity Structures 434
 - 8.4.4.4 Sub-wavelength Size Polymer LEDs 436
 - 8.4.4.5 Voltage-controlled Colours 437
- 8.5 Photoconductive and Photovoltaic Devices 439
 - 8.5.1 Introduction 439
 - 8.5.2 Mechanism of Photoconductivity in Sexithiophene 440
 - 8.5.3 Photovoltaic Applications (Solar Cells) 441
 - 8.5.4 Photovoltaic Devices Based on Polythiophenes 443
- 8.6 Electro-Optical Modulator Devices 444
 - 8.6.1 Optical Probing of Field-induced Charge in α -Sexithiophene 446

8.7	All-optical Modulator and Memory Devices	449
	References	452

9 Oligo- and Polythiophene Field Effect Transistors 459

H. E. Katz, A. Dodabalapur and Z. Bao

9.1	Introduction	459
9.2	Operation of a Field-effect Transistor	460
9.3	Modeling of Oligothiophene TFTs	461
9.3.1	Analytical Modeling	461
9.3.2	Numerical Modeling	463
9.3.3	Interface Effects	464
9.3.4	Short-channel Effects	465
9.3.5	Sub-threshold Characteristics	466
9.3.6	Energy Levels	467
9.4	Oligothiophene FETs	468
9.4.1	Synthesis and Purification	468
9.4.2	Morphology	471
9.4.3	Substituted Oligothiophenes	473
9.4.4	Fused Ring Materials	475
9.5	FETs Based on Polythiophenes	476
9.5.1	Regiorandom Polythiophene FETs	478
9.5.2	Regioregular Polythiophene FETs	478
9.5.3	All-printed Plastic FETs	481
9.6	Heterojunction FETs	483
9.7	Summary	485
	Acknowledgments	486
	References	486

10 Application of Electrically Conductive Polythiophenes 491

Gerhard Kossmehl and Gunnar Engelmann

10.1	Introduction	491
10.2	Conducting Materials	492
10.3	Antistatic Coatings	495
10.4	Electromagnetic Shielding Materials	496
10.5	Materials for Rechargeable Batteries, Capacitors	497
10.6	Junction Devices and Rectifying Bilayer Electrodes	501
10.7	Resists, Recording Materials and Fabrication of Patterns	501
10.8	Electrochromic Devices	503
10.9	Sensors	506
10.9.1	Sensors for Gases	506
10.9.2	Sensors for Ions in Aqueous Solution	507
10.9.3	Sensors for Organic Materials	508

XIV *Contents*

10.9.4	Sensors for Bio-organic Materials	512
10.10	Other Applications	512
10.10.1	General Consideration	513
10.11	Summary, Conclusions and Future Trends	516
	References	517

Index	525
--------------	------------

List of Contributors

Peter Bäuerle
Institute of Organic Chemistry II
University of Ulm
Albert-Einstein-Allee 11
D-89081 Ulm
Germany

Z. Bao
AT & T. Bell Laboratories
Lucent Technologies
600 Mountain Avenue
Murray Hill
NJ 07974
USA

D. Beljonne
Service de Chimie des Matériaux
Nouveaux
Université de Mons-Hainaut
Place du Parc 20
7000 Mons
Belgium

Jean-Luc Brédas
Service de Chimie des Matériaux
Nouveaux
Université de Mons-Hainaut
Place du Parc 20
7000 Mons
Belgium

J. Cornil
Service de Chimie des Matériaux
Nouveaux
Université de Mons-Hainaut
Place du Parc 20
7000 Mons
Belgium

Richard D. McCullough
Department of Chemistry
Carnegie Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213-2683
USA

Philippe Delannoy
Groupe de Physique des Solides
Universités Paris 6 (Pierre et Marie
Curie) et Paris 7 (Denis Diderot)
2 Place Jussieu
75251 Paris Cedex 05
France

A. Dodabalapur
AT & T. Bell Laboratories
Lucent Technologies
600 Mountain Avenue
Murray Hill,
NJ 07974
USA

Gunnar Engelmann
Institute of Organic Chemistry
Freie Universität Berlin
Tokustrasse 3
D-14195 Berlin
Germany

Denis Fichou
Laboratoire des Matériaux
Moléculaires
CNRS
2 rue Henry-Dunant
94320 Thiais
France

Richard H. Friend
University of Cambridge
Department of Physics
Cavendish Laboratory
Madingly Road
Cambridge CB3 0HE
United Kingdom

Wolfram Gebauer
C.N.R.
Istituto di Spettroscopia Molecolare
Via Castaguloi 1
40126 Bologna
Italy

Magnus Granström
University of Cambridge
Department of Physics
Cavendish Laboratory
Madingly Road
Cambridge CB3 0HE
United Kingdom

Mark G. Harrison
University of Cambridge
Department of Physics
Cavendish Laboratory
Madingly Road
Cambridge CB3 0HE
United Kingdom

Gilles Horowitz
Laboratoire des Matériaux
Moléculaires
CNRS
2 rue Henry-Dunant
94320 Thiais
France

Shu Hotta
National Institute of Materials and
Chemical Research
Japan High Polymer Center
1-1 Higashi, Tsukuba,
Ibaraki 305
Japan

Kohzo Ito
Department of Applied Physics
Faculty of Engineering
University of Tokyo
7-3-1 Hongo, Bunkyo-ku
Tokyo 113
Japan

H. E. Katz
AT & T. Bell Laboratories
Lucent Technologies
600 Mountain Avenue
Murray Hill,
NJ 07974
USA

Gerhard Kossmehl
Institute of Organic Chemistry
Freie Universität Berlin
Takustrasse 3
D-14195 Berlin
Germany

L. Lazzaroni
Service de Chimie des Matériaux
Nouveaux
Université de Mons-Hainaut
Place du Parc 20
7000 Mons
Belgium

V. Parente
Service de Chimie des Matériaux
Nouveaux
Université de Mons-Hainaut
Place du Parc 20
7000 Mons
Belgium

Carlo Taliani
C.N.R.
Istituto di Spettroscopia Molecolare
Via Castagnoli, 1
40126 Bologna
Italy

Christiane Ziegler
University of Tübingen
Institute of Physical and Theoretical
Chemistry
Auf der Morgenstelle 8
D-72076 Tübingen
Germany

Biography



Denis Fichou is a directeur de recherche at CNRS in Thiais, France. He received a Doctorat de 3^{ème} Cycle in organic chemistry at the University of Rennes, France, in 1981 and a Doctorat d'Etat in physical sciences at the University of Paris VI in 1986. He joined CNRS in 1982 at the Laboratory of Molecular Materials in Thiais. In 1986 and again in 1992, he spent two years in Tôkyô, Japan, as the CNRS Advisor of the Chemistry Department. In 1987, he initiated the successful "oligothiophenes route" at CNRS, Thiais. His current research interests focus on material chemistry and the fabrication of electronic and photonic organic devices, particularly thin film transistors and laser crystals.

List of Symbols

a	lattice constant
$\mathbf{a}$	lattice vector
C	capacitance
C	electron–continuum coupling
D	density
D	dichroism
d	thickness of sample
D	diffusion coefficient
e	electron charge
E	transition energy
E_g	intrinsic semiconductor
E_{pa}	oxidation potential
$\mathbf{F}$ or F	applied electric field
$f(E)$	Fermi function
f_r	relaxation frequency
G	charge generation
h	Planck constant
H	Hamiltonian operator
I	current
j or J	current density
J	overlap integral
$\mathbf{k}$	wave vector
k	Boltzmann constant
$K_{(\omega)}$	Kerr response function
k_{NR}	non-radiative decay rate
L	channel length
m_0	electron mass
M	dipole moment
M_N	number average molecular weight
M_W	weight average molecular weight
n	density of carriers
n	refractive index
N	number of repeat units in a chain
N	number of molecules
N_{ch}	number of injected charges
N_f	density of states at the Fermi level
N_s	number of spins
p	charge density

q	charge
r	separation between molecular centres
R	charge recombination
R	distance between sites
S	strain constant
T	temperature or absolute temperature
ν	vibrational frequency
v	velocity
V	voltage
V	intermolecular interactions
Z	number of molecules/unit cell
Z	channel width
$\Delta(r)$	distortion
Θ (cap theta)	angle between surface and molecules
Θ	Debye temperature
α	lattice constant
β	Poole–Frenkel factor
χ	susceptibility tensor
ϵ	molar absorption coefficient
ϵ	dielectric constant
ϕ	potential
ϕ_F	fluorescence quantum yield
γ	cubic nonlinearity
η	internal quantum efficiency
κ	absorption coefficient
λ	mean free path
$\lambda_{\max}$	wavelength of absorption
μ	mobility
ν	band maximum
θ	fraction of charges free to move
ρ	resistivity
σ	conductivity
τ	relaxation time
ω	optical phonon frequency
$\psi_{\mathbf{r}}$	polaron wave function
Φ	wave function
Φ	fluorescence

List of Abbreviations

acac	acetylacetonate
AFM	atomic force microscopy
AM1	Austin model 1
BBN	9 borabicyclo[3.3.1]nonane
BCB	benzocyclobutene
BZ	Brillouin zone
CASSCF	Complete active space self-consistent field
CASPTZ	Multiconfiguration second-order perturbation theory
CB	conduction band
CI	configuration interaction
CNDO/CI	complete neglect of differential overlap/configuration interaction
cod	cyclooctadiene
CTE	charge transfer electrons
CV	capacitance–voltage
CV	cyclic voltammetry
DDQ	dichlorodicyanoquinone
DFT	density functional theory
DFWM	degenerate four wave mixing
DMAC	<i>N,N'</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
dmso	dimethyl sulfoxide
DOS	density of states
dppp	1,3-diphenylphosphinopropane
EDOT	3,4-ethylenedioxythiophene
EFISH	electronic field induced second harmonic generation
EL	electroluminescenc
ELS	electron energy los
EPR	electron paramagnetic resonance
ESR	electron spin resonance
EVS	electrochemical voltage spectroscopy
FEBS	frequency domain electric birefringence spectroscopy
FET	field effect transistor
FTIR	Fourier transform infrared
GPC	gel phoresis chromatography
HB	herringbone
HCM	hydroquinonemethylether
HH	head-to-head (coupling)
HOMO	highest occupied molecular orbital
HOPG	highly oriented pyrolytic graphite

HPLC	high pressure liquid chromatography
HREELS	high resolution energy electron loss spectroscopy
HT	head-to-tail (coupling)
HV	high vacuum
INDO	intermediate neglect of differential overlap
IR	infrared
ISC	inter system crossing
ITO	indium-doped tin oxide
L.R.	Lawesson's reagent
LDA	lithium diisopropylamide
LED	light emitting diodes
LEED	low energy electron diffraction
L.R.	Lawesson's Reagent
LSDA	local spin density approximation
LUMO	lowest unoccupied molecular orbital
M-I	metal-insulator
MIS	metal-insulator-semiconductor
MNDO	modified neglect of differential overlap
MO	molecular orbital
MOS	metal-oxide-semiconductor
MP2	Möller-Plesset perturbation theory
MRD-CI	multi reference double configuration interaction
NBS	<i>N</i> -bromosuccinimide
NEXAFS	near edge X-ray absorption fine structure
NLO	nonlinear optics
NMP	1-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
OASLM	optically-addressed SLM
ODMR	optically detected magnetic resonance
OFET	organic FET
OLED	organic LED
P3-BTSNa	sodium poly(3-thiophene- β -butanesulfonate)
P3-ETSNa	sodium poly(3-thiophene- β -ethanesulfonate)
P3-TPSNa	sodium poly(3-(3-thienyl)propanesulfonate)
PAT	poly(3-alkylthiophene)
PBD	2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole
PBT	poly(3-butylthiophene)
PC	photoconductivity
PC	propylene carbonate
PCHMT	poly(3-cyclohexyl-4-methylthiophene)
PCHT	poly(3-cyclohexylthiophene)
PDBBT	poly(4,4'-dibutyl-2,2'-bithiophene)
PDDT	poly(3-dodecylthiophene)
PDDUT	poly(3-(2-(<i>N</i> -dodecyl-carbamoyloxy)ethyl)thiophene)
PDHBT	poly(3,3'-dihexyl-2,2'-bithiophene)
PDOBT	poly(4,4'-dioctyl-2,2'-bithiophene)

PDT	poly(3-decylthiophene)
PEDOT	poly(3,4-ethylenedioxythiophene)
PHT	poly(3-hexylthiophene)
PiBT	poly(3-isobutylthiophene)
PL	photoluminescence
PLED	polymer light emitting diodes
PMMA	polymethylmethacrylate
PMT	poly(3-methylthiophene)
POPT	poly(4-octylphenyl)thiophene
POT	poly(3-octylthiophene)
PPV	poly(<i>p</i> -phenylenevinylene)
PT	polythiophene
PTOPT	poly[3-(4-octylphenyl)2,2'-bithiophene]
PVK	poly(9-vinyl carbazole)
RI	refractive index
ROHF	restricted open shell Hartree–Fock
RPE	electron paramagnetic resonance
SAM	self-assembled monolayer
SCF	self consistent field
SCLC	space-charge limited current
SCRf	self consistent reaction field
SE	stimulated emission
SERS	surface enhanced Raman spectroscopy
SFM	scanning force microscopy
SHG	second harmonic generation
SLM	spatial light modulators
SOMO	singly occupied molecular orbital
SNOM	scanning nearfield optical microscopy
SSH	Su, Schrieffer and Heeger
STM	scanning tunneling microscopy
TCNQ	7,7,8,8-tetracyanoquinodimethane
TEB	transient electric birefringence
TFT	thin film transistor
THF	tetrahydrofuran
THG	third harmonic generation
THP	tetrahydropyranyl
TMS	trimethylsilyl
TOF	time of flight
TPE	two photon excitation
TT	tail-to-tail (coupling)
UHV	ultra high vacuum
UPS	UV photoelectron spectroscopy
UV	ultraviolet
VB	valence band
VEH	valence effective Hamiltonian
Vis	visible

Vis	visible
VRH	variable range hopping
XRD	X ray diffraction

1 The Chemistry of Conducting Polythiophenes: from Synthesis to Self-Assembly to Intelligent Materials

Richard D. McCullough

1.1 Introduction

In the late 1970s, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of electronic and optical devices. It now appears with the discoveries of, for example, polymer light emitting diodes (LEDs) [1] and organic transistors [2] that new technologies are eminent. Polythiophenes are an important representative class of conjugated polymers that form some of the most environmentally and thermally stable materials that can be used as electrical conductors, non-linear optical devices, polymer LEDs, transistors, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, batteries, nano-switches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices [3, 4]. Polythiophene and its derivatives work very well in some of the above applications and less impressively in other devices. Creative new design and development strategies of new polythiophenes has led to captivating new materials and enhanced performance in certain devices. The ability of molecular designers to begin to understand how to gain control over the structure, properties, and function in polythiophenes continues to make the synthesis of polythiophenes a critical subject in the development of new advanced materials. Here we attempt to review the synthesis of polythiophenes comprehensively. Due to the enormous literature on the synthesis of polythiophenes, we are sure that excellent work in this area will be inadvertently overlooked. However, we will highlight both the pioneering work and the frontier in the synthesis of polythiophenes.

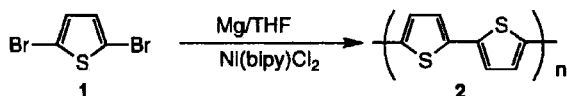
It is important to realize that, as it has become clear that structure plays a dominant role in determining the physical properties of conducting polymers, more research has focused on directing structure and function of these materials with synthesis. Synthesis can help to determine the magnitude of π overlap along the backbone and eliminate structural defects. Materials assembly (and/or processing) determines interchain overlap and dimensionality. Planarization of the backbone and assembly of the backbone in the form of π stacks lead to better materials and enhanced device performance in almost every category ranging from electrical conductivity to stability. Therefore, both remarkable enhancements in the electronic and photonic properties of the resultant materials and the creation of new functions,

such as new sensory materials, critically depends on the synthesis of the polythiophene. This of course leads to the exciting prospect that the properties of polythiophenes can be selectively engineered through synthesis and assembly. A large portion of both the pioneering and future work in conjugated polymers strongly depends on synthetic chemists creating new polymers that can be fabricated into new devices and whose physics and chemistry can be deeply understood.

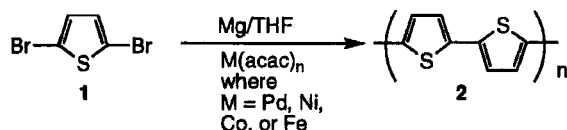
1.2 Chemical synthesis of unsubstituted polythiophene (PT)

One of the first chemical preparations of unsubstituted polythiophene (PT) was reported in 1980 by two groups [5, 6]. Both synthesized polythiophene by a metal catalyzed polycondensation polymerization of 2,5-dibromothiophene (Scheme 1). Yamamoto's synthesis treats 2,5-dibromothiophene (**1**) with Mg in THF in the presence of nickel(bipyridine) dichloride. The Mg reacts with either bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene, which is self-coupled with the Ni(II) catalyst to form a thiophene dimer carrying a MgBr at one end and a Br at the other. This condensation reaction is propagated and eventually low molecular weight PT is formed. The polymerization is the extension of Kumada coupling of Grignard reagents to aryl halides [7]. Since PT, even at low molecular weights, is insoluble in THF, the precipitation of the polymer under the above reaction conditions limits the formation of higher molecular weights. The PT synthesized by this method leads to 78% insoluble polymer that does not melt. The soluble fraction is lower molecular weight oligomers. Polythiophene polymer of molecular weight greater than 3000 are not soluble in hot chloroform [8]. The elemental analysis of this polymer indicated 1–3% Mg remains in the polymer sample. Similar results were found by Lin and Dudek. Polymerization of 2,5-dibromothiophene in the presence of Mg in THF using either

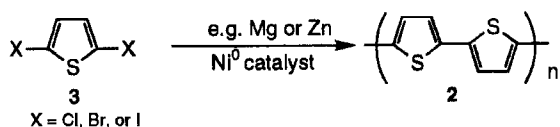
Yamamoto Route



Lin and Dudek Route



Scheme 1. The first chemical syntheses of polythiophene.

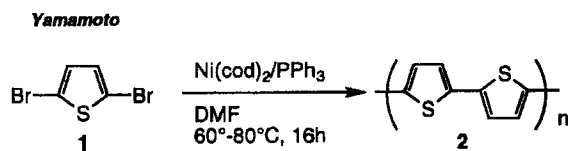
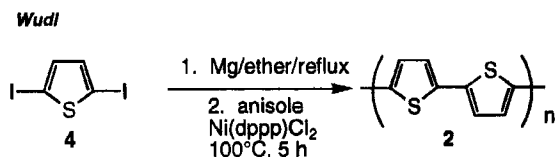


Scheme 2. Polycondensation dehalogenation route to polythiophene.

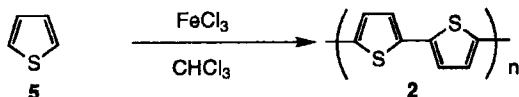
palladium(acac)₂ (acac = acetylacetonate) or Ni(acac)₂ or Co(acac)₂ or Fe(acac)₃ catalyst yields low molecular weight PT containing at 3% impurities as determined by elemental analysis.

Polymerization of 2,5-dihalothiophene can be accomplished by reacting the generated bromo-Grignard of thiophene with Ni(II) catalyst such as Ni(dppp)Cl₂ (dppp = 1,3-diphenylphosphinopropane) or the 2,5-dihalothiophene can be polymerized by a polycondensation dehalogenation reaction with Ni(0) (Scheme 2). Systematic studies of the polymerization of 2,5-dihalothiophene (**3**) have subsequently been done by primarily Yamamoto [8–12] and others [13–15]. Varying the amounts of Mg [13], the solvent [10, 14, 15], the type of metal (i.e. Mg, Zn, etc.) [10], concentration of monomer [13], the type halogen on the monomer [8, 12–15], the temperature [8, 9, 12], reaction time [8], and the type of catalyst used [8–13] has led to some good chemical methods for the synthesis of PT. The extension of these chemical methods to the synthesis of poly(3-alkylthiophene)s (PATs) and other polythiophenes will be later noted.

It is seen in a paper by Wudl [14] that very good samples of PT can be prepared by the polymerization of highly purified 2,5-diiodothiophene (Scheme 3). First 2,5-diiodothiophene (**4**) is reacted with Mg in ether at reflux. The preformed



Sugimoto and Yoshino



Scheme 3. Specific examples of the synthesis of polythiophene.

iodomagnesioiodothiophene is isolated as a residue and redissolved in hot anisole, whereupon Ni(dppp)Cl_2 is added and the mixture heated at 100°C for 5 h to induce polymerization. Extensive washing of the isolated PT with methanol, chloroform, THF, and chlorobenzene leads to the isolation of PT with elemental analysis within 0.3% of the calculated values for $\text{C}_{188}\text{H}_{97}\text{IS}_{46}$ (molecular weight $\approx 4\text{K}$ or 46 thiophene rings and 1 butadiene unit). This high purity PT sample contains barely 50 ppm of Mg and Ni. However, it is proposed that the one butadiene unit arises from a desulfurization reaction promoted by Ni(0) intermediates [7]. Polymerization of the 2,5-dibromothiophene yielded PT that analyzed 2–3% low in sulfur, apparently due to said desulfurization. The Wudl sample of PT was characterized by IR, ESR, conductivity and thermopower measurements. The conductivity of the AsF_5 -doped material was about 10 S cm^{-1} .

Work on the polycondensation polymerization of 2,5-dihalo thiophenes by Yamamoto has shown that essentially a quantitative yield of PT can be made from 2,5-dibromothiophene, Ni(cod)_2 (cod = cyclooctadiene), and PPh_3 at $60\text{--}80^\circ\text{C}$ in DMF (Scheme 3) [8]. It is also reported that the percentage of Br end groups decreases as reaction times are increased from 8 to 16 h, indicating that perhaps some seemingly insoluble PT continues to grow. Both less active catalysts such as $\text{Ni(PPh}_3)_4$ and less active monomers such as 2,5-dichlorothiophene lead to lower yields of PT. The PT synthesized is exclusively coupled at the 2,5-carbons as indicated by solid state ^{13}C NMR which exhibits peaks at 136 and 125 ppm only. Other synthetic methods can produce the conjugation disrupting 2,4-coupled polythiophene structure. While the elemental analyses for carbon and hydrogen are within 0.3%, the sulfur content of the PT is off by 3%. Vacuum deposition of PT (estimated molecular weight of 1.5–2K) onto carbon, gold, KBr, or aluminum at $250\text{--}300^\circ\text{C}$ at 10^{-4} Pa can be accomplished. Electron diffraction patterns of PT on carbon indicates the formation of crystalline PT with the PT chains arranged perpendicular to the carbon substrate — similar to oligothiophene films. Vacuum deposition of PT on rubbed polyimide films gave PT chains oriented parallel to the polyimide substrate with a dichroic ratio of 1.5. The PT films are further characterized by IR, X-ray, and conductivity measurements. Powder conductivity measurements on iodine doped samples gave a maximum conductivity of 50 S cm^{-1} .

Although the above methods have been generally used to prepare high quality PT (and PATs), other methods have been reported. An early report by Sugimoto reported the synthesis of PT by treating thiophene (**5**) with FeCl_3 (Scheme 3). The treatment of thiophene with butyl lithium provides 2,5-dilithiothiophene that can be polymerized with CuCl_2 [16]. Thiophene can also be polymerized by trifluoroacetic acid in the presence of thallium(III) trifluoroacetate [17]. The acid-induced polymerization of thiophene was reported as early as 1883, yet produced tetrahydrothiophene units [18]. A novel polymerization of thiophene vapor can produce encapsulated PT in transition metal-containing zeolites [19].

Despite the lack of processability, the expected high temperature stability [14] and potential for very high electrical conductivity of PT *films* (if made) still make it a highly desirable material. Perhaps precursor routes to PT will eventually lead to processable PT films.