Denis Fichou

Handbook of Oligo- and Polythiophenes

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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

Printed on acid-free and chlorine-free paper

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 luminophores 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

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Biography

Denis Fichou is a directeur de recherche at CNRS in Thiais, France. He received a Doctorat de 3ème 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 enegry
E_{g}	intrinsic semiconductivity
E_{pa}	oxidation potential
$\mathbf{F}$ or F	applied electric field
$\mathrm{f}(E)$	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
v	vibrational frequency
v	velocity
V	voltage
V	intermolecular interactions
Z	number of molecules/unit cell
Z	channel width
Δ(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
λ_{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
ψr	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	*N*,*N*′-dimethylacetamide
DMF	*N*,*N*-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 configuraton interaction
NBS	*N*-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-biphenylyl)-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-(*N*-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(*p*-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

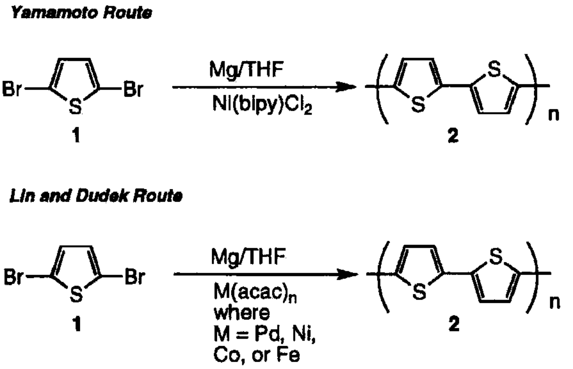
1.1 Introduction

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, nanoswitches, 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.

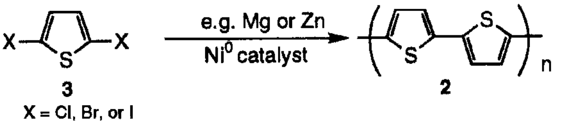
It is important to realize that, as it has become clear that structure plays a dominant role in determining the physical properties of conducting polymers, more research has focused on directing structure and function of these materials with synthesis. Synthesis can help to determine the magnitude of 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



Scheme 1. The first chemical syntheses of polythiophene.

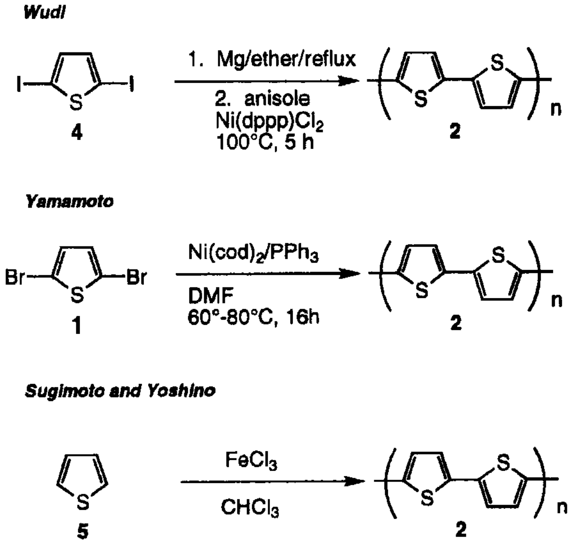


Scheme 2. Polycondensation dehalogenation route to polythiophene.

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)Cl$_2$ (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



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 $C_{188}H_{97}IS_{46}$ (molecular weight ≈4K 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-dihalothiophenes 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 60–80°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 $Ni(PPh_3)_4$ 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 250–300°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.