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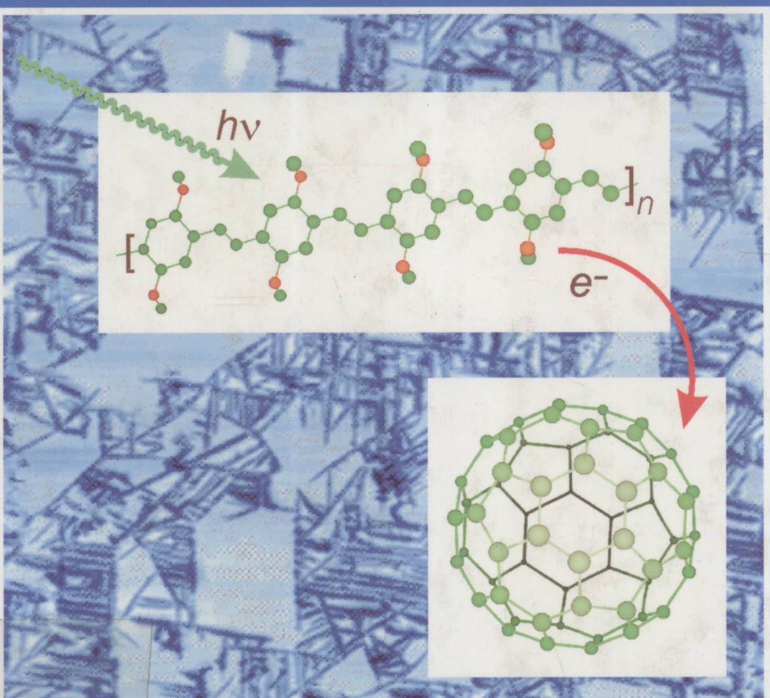
Semiconducting Polymers

Chemistry, Physics and Engineering

Edited by
G. Hadziioannou and P. F. van Hutten



Georges Hadziioannou, Paul F. van Hutten (Eds.)

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Preface

When writing about a subject from a rapidly evolving research area, one is tempted into dealing with the latest results, those that still fascinate. This is dangerous, however, for such findings may not have a lasting value. They may not be sufficiently unambiguous, enlightening, or novel to deserve their place in a reference work.

We have invited our colleagues to write about their field of expertise, and put down on paper the things that they are really comfortable with, and confident of. Fortunately, we found many willing to contribute in this vein. With their help, we have been able to collect much of the base of knowledge that has been gathered in a decade of research on semiconducting polymers. It is recognized, of course, that research in this field could build on what had been learned about conducting polymers in the preceding decade.

We like to thank those who collaborated in this book project. This includes all authors, as well as the people at Wiley-VCH who offered us the opportunity and made it become a reality.

Georges Hadziioannou
Paul van Hutten

Groningen, September 1999

Foreword

The science and technology of conducting polymers are inherently interdisciplinary; they fall at the intersection of three established disciplines: chemistry, physics and engineering; hence the name for this volume. These macromolecular materials are synthesized by the methods of organic chemistry. Their electronic structure and electronic properties fall within the domain of condensed matter physics. Efficient processing of conjugated polymer materials into useful forms and the fabrication of electronic and opto-electronic devices require input from engineering; i. e. materials science (more specifically, polymer science) and device physics.

With the emergence of semiconducting and metallic polymers as an interdisciplinary field, a host of new concepts have evolved which are of broad and fundamental importance. The field originated in the 1970s with an initial focus on n-type and p-type doping of conjugated polymers. Reversible doping of semiconducting polymers was the early highlight with associated electrical conductivity values that span the full range from insulator to metal. The unique electrochemistry of conducting polymers was subsequently discovered and remains as an active area of science and technology.

The opportunity to synthesize new conjugated polymers with improved properties began to attract the attention of a larger number of synthetic chemists in the 1980s. Equally important was the subsequent development of stable, processible metallic polymers. As a result of these efforts, we now have a class of materials which exhibit a unique combination of properties: *the electronic and optical properties of metals and semiconductors in combination with the processing advantages and mechanical properties of polymers.*

Because of the progress toward higher purity, processible semiconducting polymers, these materials are now available for use in "plastic electronic" devices. In this context, the discovery (at Cambridge University) of electroluminescence from semiconducting, conjugated polymers, was of particular importance. More generally, however, plastic electronics devices include diodes, photodiodes, photovoltaic cells, sensors, light-emitting diodes, lasers, field effect transistors and all-polymer integrated circuits – and the list is growing. Thus, the emergence of electronic and opto-electronic devices fabricated from semiconducting polymers has been a principal focus of the 1990s.

Despite the scientific progress and the demonstration of novel device concepts, there was considerable skepticism that semiconducting polymers would ever reach the levels of purity required for long-lifetime commercial devices. In the context of the last 50 years of semiconductor physics, conjugated polymers were often considered as "dirty" and poorly characterized materials. Therefore, the recent demonstration of high-brightness polymer emissive displays with operating lifetimes of 10000–20000 hours was a particularly important step; it is now clear that semiconducting polymers can be used to fabricate consumer products that meet commercial specifications.

As a result of the remarkable progress in the chemistry, physics and engineering (device physics) of semiconducting and metallic polymers, we are now witnessing the beginning of a revolution in "Plastic Electronics".

The field of semiconducting and metallic polymers remains vital; again and again the science and technology have moved into new directions. Specific examples of recent advances (within the 1990s) of special importance include the following:

- Metallic polymers which are stable, soluble and processible, and therefore suitable for industrial applications;
- The science and technology of high-efficiency light emission from polymer light-emitting diodes and polymer light-emitting electrochemical cells;
- Ultrafast photoinduced electron transfer in semiconducting polymers mixed with controlled amounts of acceptors; this phenomenon has opened the way to a variety of applications including high-sensitivity plastic photodiodes, and efficient plastic solar cells;
- Semiconducting polymers as materials for solid-state lasers.

This book, "Semiconducting Polymers – Chemistry, Physics and Engineering", edited by Georges Hadziioannou and Paul van Hutten of the University of Groningen (The Netherlands) summarizes progress in areas of current activity within the field. The various chapters, all contributed by leading researchers, provide a summary and review of the field that will be useful and important to anyone seeking a strong background in the basic interdisciplinary science and an up-to-date "snapshot" of the current status of research. Emphasis is on the basic physics and chemistry of conjugated polymers as electronic and opto-electronic materials and on the performance (status, opportunities and limitations) of the electronic and opto-electronic devices that are responsible for the on-going revolution in "Plastic Electronics".

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List of Abbreviations

ε	dielectric constant
AFM	Atomic Force Microscopy
AOM	acousto-optic modulator
ASE	amplified spontaneous emission
BDAD	*bis*-(4′-diphenylaminostyryl)-2,5-dimethoxybenzene
BEH-PPV	poly(2,5-bis(2′-ethylhexyloxy)-*para*-phenylene vinylene)
BuEH-PPV	poly(2-butyl-5-(2′-ethylhexyl)-1,4-phenylene vinylene)
CB	conduction band
CEO	coupled electronic oscillator
CP	conducting polymer
CPG	charge photogeneration
CTE	charge-transfer excitons
CW	Continuous Wave
DASMB	diphenylaminostyrylbenzene
DAT	di-*para*-anisyl-*para*-tolylamine
DBR	distributed Bragg reflector
DFB	distributed feedback
DH6T	dihexyl-substituted 6T
DHPPV	poly(2,5-diheptyl-*para*-phenylene vinylene)
DIA	doping-induced absorption
DOO-PPV	poly(2,5-dioctyloxy-*para*-phenylene vinylene)
DOS	distribution of states
DOS	density-of-states
DOVS	density of valence states
DPOP-PPV	poly(1,4-phenylene-1,2-diphenoxyphenylvinylene)
DSC	Differential scanning calorimetry
DT	differential transmission
DTA	di-*para*-tolyl-*para*-anisylamine
EA	electroabsorption
ECC	external color conversion
ED	electron diffraction
EDC	energy distribution curve
EL	Electroluminescence
ESCA	Electron Spectroscopy for Chemical Application
ESR	electron spin resonance
FET	field-effect transistor

FGM	Fluctuating Gap Model
FN	Fowler-Nordheim
FTO	fluorine-doped tin dioxide
FWHM	full width at half maximum
GP	geminate pair
GPC	Gel Permeation Chromatography
HOMO	highest occupied molecular orbital
H-T	Herzberg-Teller
HV	high vacuum
ICC	internal color conversion
IGFET	insulated gate FET
INDO	Intermediate Neglect of Differential Overlap
IPCE	incident photon to converted electron
IRAV	infrared active vibrational modes
ISC	intersystem crossing
ITO	indium-tin oxide
LB	Langmuir-Blodgett
LCD	liquid crystal display
LEC	light-emitting electrochemical cell
LED	light-emitting diode
LESR	Light-Induced Electron Spin Resonance
LPPP	laddered poly(*para*-phenylene)
LUMO	lowest unoccupied molecular orbital
MBE	molecular beam epitaxy
MEH-DSB	2-methoxy-5-(2′-ethylhexyloxy)-1,4-bis(4-styrylstyryl)benzene
MEH-PPV	Poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene
MeLPPP	methyl-substituted poly(*para*-phenylene)-type ladder polymer
MIM	a metal/insulator/metal
MIMIC	micromolding in capillary
MIS	metal-insulator-semiconductor
MISFET	metal-insulator-semiconductor FET
m-LPPP	methyl-substituted poly(*para*-phenylene)-type ladder polymer
MNDO	Modified Neglect of Diatomic Overlap
MOSFET	silicon metal-oxide-semiconductor FET
MS	metal-semiconductor
MSA	tris(*p*-methoxystilbene)amine
MSM	metal/semiconductor/metal
MTR	multiple trapping and thermal release
NBS	*N*-bromosuccinimide
NTCDA	naphthalene tetracarboxylic dianhydride
ODMR	optically detected magnetic resonance
OFET	organic field-effect transistor
OGM	oriented gas model
OLED	organic light-emitting diodes
OMA	optical multichannel analyzer
OMBD	organic molecular beam deposition

OPV	oligo(phenylene vinylene)
P3HT	poly(3-hexylthiophene)
P3OT	poly(3-octylthiophene)
PA	photoinduced absorption
PADMR	PA-detected magnetic resonance
PAH	polyaromatic hydrocarbon
PAni	polyaniline
PB	photobleaching
PBD	2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole
Pc	Phthalocyanine
PD	photodiode
PDA	personal digital assistant
PDOT	poly(dodecyloxy-terthienyl)
PTCDA	perylene tetracarboxylic dianhydride
PEDOT-PSS	poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PEDT	poly(ethylenedioxythiophene)
PEOPT	poly(3-(4′-(1″,4″,7″-trioxaoctyl)-phenyl)thiophene)
PES	photoelectron spectroscopy
PF	Poole-Frenkel
PHP	*para*-hexaphenyl
PIA	photoinduced absorption
PL QY	photoluminescence quantum yield
PLDMR	PL-detected magnetic resonance
PM	photomodulation spectroscopy
PMMA	polymethylmethacrylate
PP3VE	copolymer containing phenylene, vinylene and non-conjugated ethylidene units
PPP	poly(*para*-phenylene)
PPPV	poly(phenylphenylene vinylene)
PPV	poly(*para*-phenylene vinylene)
PS	polystyrene
PSD	power spectral density
PT	polythiophene
PTFE	polytetrafluoroethylene
PTV	poly(2,5-thienylenevinylene)
PVK	polyvinylcarbazole
r.m.s.	root mean square
RS	Richardson-Schottky
SCI	single configuration interaction
SCLC	space charge limited current
SE	stimulated emission
SF	superfluorescence
Si-PPV	poly(dimethylsilylene-*para*-phenylenevinylene-(2,5-di-*n*-octyl-*para*-phenylene)-vinylene-*para*-phenylene)
STM	scanning tunneling microscopy
TAA	tri-*para*-anisylamine

TCNQ	tetracyanoquinodimethane
TDAE	tetrakisdimethylaminoethylene
TE	transverse electric modes
TEM	transmission electron microscopy
TFT	thin-film transistor
TM	transverse magnetic modes
TOF	time of flight
TPA	two-photon absorption
TTA	tri-*para*-tolylamine
UHV	ultra-high vacuum
UPS	Ultraviolet Photoelectron Spectroscopy (UPS)
UV	ultraviolet
VB	valence band
VEH	Valence Effective Hamiltonian
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction

Contents