# Conducting Polymers, Fundamentals and Applications

## A Practical Approach

Prasanna Chandrasekhar

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## *A Practical Approach*

*by*



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# CONDUCTING POLYMERS, FUNDAMENTALS AND APPLICATIONS
## *A Practical Approach*

«Yad bhaavi, tad bhaavi,
yadabhaavi, na tad anyathaa»

*esha upadesha:a; eshaevamcha aadesha:a;*
*evamcha upaasitavyam;*
*iti Prasannena vilambita shikshyam.*

*Dedicated to My Parents*

# LIST OF COMMON ABBREVIATIONS

The abbreviations listed below are classified into the following categories:

*General*
*Common Conducting Polymers*
*Other Polymers*
*Monomers*
*Dopants*
*Chemicals, Solvents*
*Techniques, Methodology*

| ***Abbreviation*** | ***Explanation*** |
|---|---|
| *General*: | |
| **CP** | **Conducting Polymer** |
| AC | Alternating Current |
| ASTM- | Testing or other standard issued by American Society for Testing and Materials |
| CB | Conduction Band |
| CON1/2/3 | $1^{st}$, $2^{nd}$, $3^{rd}$ configurations used in Ashwin electrochemical devices |
| DC | Direct Current |
| EA | Electron Affinity |
| e-beam | Electron-Beam |
| $E_F$ | Fermi level (primarily in context of semiconductors) |

| ***Abbreviation*** | ***Explanation*** |
|---|---|
| $E_g$ | E(gap), Band Gap Energy |
| EMI | Electromagnetic Interference |
| EMI-SE | Electromagnetic Interference Shielding Effectiveness |
| EO, E/O, E-O | Electro-Optic(al) |
| ESD | Electrostatic Discharge |
| FET | Field Effect Transistor |
| FWHM | Full Width at Half Maximum (peak half-width) |
| HOMO | Highest Occupied Molecular Orbital |
| H-T | Head-to-Tail (coupling) |
| $I_p$, IP | Ionization Potential |
| ITO | Indium-Tin-Oxide |
| I-V | Current-Voltage (curves, etc.) |
| LC | Liquid Crystal(s) |
| LCD | Liquid Crystal Display |
| LEC | Light-Emitting Electrochemical Cell(s) |
| LED | Light Emitting Diode |
| LUMO | Lowest Occupied Molecular Orbital |
| MIL-, MIL-C-, MIL-STD- | Military Standards issued by US Dept. of Defense |
| MWt, MW | Molecular weight |

| Abbreviation | Explanation |
|---|---|
| PV | Photovoltaic(s) |
| RCS | Radar Cross Section |
| S, S/cm | Siemen, Siemen/cm (Siemen, unit of Impedance, = $\Omega^{-1}$) |
| SC | Semiconductor |
| SCALE | Symmetrically Configured Alternating Current Light Emitting |
| SCE | Saturated Calomel Electrode |
| VB | Valence Band |

*Common Conducting Polymers*:

| | |
|---|---|
| BBB | *see p. 423* |
| BBL | *see p. 423* |
| PBT | *see p. 423* |
| P(....) | Poly(....) |
| P(Ac) | Poly(acetylene(s)) |
| P(ANi), PANI, PAN | Poly(aniline) |
| P(DiAc) | Poly(di-acetylene(s)) |
| PPO | *see p. 423* |
| P(PO), PPO | Poly(*p*-phenylene-oxide) |
| P(PP), PPP | Poly(*p*-phenylene) |
| P(PS), PPS | Poly(*p*-phenylene-sulfide) |
| P(PV), PPV | Poly(*p*-phenylene-vinylene) |
| P(Pyr), P(Py) | Poly(pyrrole) |
| PSS | Poly(styrene sulfonate) |
| P(T) | Poly(thiophene) |
| P(TV), PTV | Poly(thienylene vinylene) |
| P(3AT), P(AT) | Poly(3-alkyl thiophenes) |
| P(3DDT), P(DDT), PDDT | Poly(3-dodecyl thiophene) |
| P(3HT), P(HT) | Poly(3-hexyl thiophene) |

Abbreviation Explanation

| | |
|---|---|
| P(3MT), P(3MeT) | Poly(3-methyl thiophene) |
| P(3OT), P(OT) | Poly(3-octyl thiophene) |

*Other Polymers*:

| | |
|---|---|
| HDPE | H[illegible]y Poly(ethylene) |
| LDPE | [illegible]ity Poly(ethylene) |
| PAMPS | [illegible]crylamido-2-methyl-1-propane-su[illegible]c acid) |
| PE | Poly(ethylene) |
| PEG | Poly(ethylene glycol) |
| PEMA | Poly(ethyl methacrylate) |
| PEO | Poly(ethylene oxide) |
| PET | Poly(ethylene terephthalate) |
| PMMA | Poly(methyl methacrylate) |
| PSS(A) | Poly(styrene sulfonate), Poly(styrene sulfonic acid) |
| PVA | Poly(vinyl alcohol) |
| PVB | Poly(vinyl butyral) |
| PVC | Poly(vinyl chloride) |
| PVCz | Poly(vinyl carbazole) |
| PVS | Poly(vinyl sulfate) |

*Monomers*:

| | |
|---|---|
| 4ABP | 4-amino biphenyl |
| ANi | Aniline |
| AT, 3-AT | 3-alkyl thiophene |
| DPA | Diphenyl amine |
| DPBz | *N, N'*-diphenyl benzidine |
| MT, MeT, 3-Me-T | 3-methyl thiophene |
| PV | *p*-phenylene-vinylene |
| Py, Pyr | pyrrole |
| T | thiopene |
| TV | Thienylene Vinylene |

***Abbreviation*** ***Explanation***

*Dopants*:

| | |
|---|---|
| PSS | Poly(styrene sulfonate) |
| PVS | Poly(Vinyl Sulfonate/Sulfate) |
| Tos, TOS | *p*-Toluene-Sulfonate (Tosylate) |
| Trifl | Trifluoromethane Sulfonate (Tosylate) |

*Chemicals, Solvents*:

| | |
|---|---|
| DMF | *N,N'*-Dimethyl Formamide (solvent) |
| Et | Ethyl |
| GBL, γ-BL | Gamma-Butyro Lactone (solvent) |
| Me | Methyl |
| PC | Propylene Carbonate (solvent) |
| THF | Tetra-Hydro Furan (solvent) |

*Techniques/Methodology*:

| | |
|---|---|
| AFM | Atomic Force Microscopy |
| CA | Chronoamperometry |
| CC | Chronocoulometry |
| CV | Cyclic Voltammogram |
| CVA | Chronovoltabsorptometry |
| DFWM | Degenerate Four-Wave Mixing |
| DPV | Differential Pulse Voltammetry |
| DSC | Differential Scanning Calorimetry |
| EELS | Electron Energy Loss Spectroscopy |

| ***Abbreviation*** | ***Explanation*** |
|---|---|
| EH | Extended Hückel |

| | |
|---|---|
| EIS | Electrochemical Impedance Spectroscopy |
| EL | Electroluminescence |
| ENDOR | Electron Nuclear Double Resonance (spectroscopy) |
| EPR | Electron Paramagnetic Resonance (spectroscopy) |
| EQCMB | Electrochemical Quartz Crystal MicroBalance |
| ESR | Electron Spin Resonance (spectroscopy) |
| FIA | Flow Injection Analysis |
| GC | Gas Chromatography |
| GPC | Gel Permeation Chromatography |
| IR | Infrared |
| LB | Langmuir-Blodgett (film forming technique) |
| LWIR | Long-Wave Infrared |
| MWIR | Medium-Wave Infrared |
| MAS | Magical Angle Spinning (used in NMR spectroscopy) |
| MS | Mass Spectrometry |

| ***Abbreviation*** | ***Explanation*** |
|---|---|
| Nd:YAG | Neodymium:Yttrium-Aluminum-Garnet (laser, ca. 1.06 $\mu$m) |

| | |
|---|---|
| NLO | Non-Linear Optic(al, s) |
| NPV | Normal Pulse Voltammetry |
| NMR | Nuclear Magnetic Resonance (spectroscopy) |
| OCM | Open Circuit Memory (Optical Memory Retention) |
| PIA | Photo-Induced Absorption |
| PIB | Photo-Induced Bleaching |
| PL | Photo-Luminescence |
| QCM | Quartz Crystal Microbalance |
| (%-)R | %-Reflectance |
| RBS | Rutherford Backscattering |
| SEM | Scanning Electron Microscopy |
| SPEL | Spectroelectrochemical Data, Spectro-electrochemical characterization curves |
| SSH | Su-Schrieffer-Heeger (Hamiltonian) |
| STM | Scanning Tunneling Microscopy |
| (%-)T | %-Transmission |
| TGA | Thermogravimetric Analysis |
| THG | Third Harmonic Generation |
| ***Abbreviation*** | ***Explanation*** |
| TPA | Two-Photon Absorption |
| UV-Vis | Ultra-Violet-Visible (spectral region) |

| | |
|---|---|
| VEH | Valence Effective Hamiltonian |
| Vis | Visible (spectral region) |
| VRH | Variable Range Hopping (Conduction Model) |
| XPS | X-Ray Photoelectron Spectroscopy |
| XRD | X-Ray Diffraction |
| Z-N | Ziegler-Natta (polymerization process) |

# FOREWORD

## *by Lawrence Dalton*

Like semiconductors, organic materials with extended π-electron conjugation (e.g., "Conducting Polymers") can give rise to novel electrical, optical, and magnetic phenomena. Like semiconductor materials, such phenomena can, at least hypothetically, be translated into a variety of useful devices. However, organic π-electron materials, unlike semiconductors, are not atomic solids but rather are typically amorphous polymeric materials. Phenomena such as charge transport in organic materials can be quite different (e.g., variable range hopping) from that encountered in semiconductors and a range of mechanisms can be active depending on material processing. Possible "Conducting Polymer" structures and processing protocols are almost limitless. Certainly, the possibilities for "molecular engineering" of Conducting Polymers are very large indeed. The construction of devices such as light emitting diodes and non linear optical switches involve quite different considerations when using π-electron materials compared to construction of such devices from semiconductors. Not only are potential applications of π-electron polymeric materials very impressive in terms of anticipated economic impact of specific applications, but the anticipated range of applications is very large (e.g., light emitting diodes, batteries, sensors, photorefractive devices, electro- and photochromic devices and materials, microwave absorbing materials, second and third order nonlinear optical materials and devices, etc.).

The field of "Conducting Polymers" has been very dynamic in its evolution. From simple-minded pictures of bond alternation defects and application to the development of light weight batteries, the field has evolved to include an ever-widening area of topics and applications. In recent years, applications involving electroluminescence, photorefractivity, electrochromism, optical nonlinearity, and sensing have particularly attracted attention. The literature for each application area has become enormous (e.g., thousands of articles published on single topics such as organic light emitting diodes). Because of the vastness and diversity of the journal and conference proceedings literature related to the topic of Conducting Polymers, a text written from the perspective of a single individual is particularly useful as an educational tool for acquainting scientists with various aspects of this topic.

The importance of the topics covered in the current text certainly recommends this work to the scientific community.

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# PREFACE

This book addresses the critical need for a primarily pedagogical and instructional text in Conducting Polymers (CPs) at a very basic level, which remains as yet unfulfilled. Such a book should be capable of being used by a very wide variety of researchers and students in the very varied and multidisciplinary fields, in which CPs have recently found application.

The present book emanated from a short course taught by the author at the July 1995 San Diego, CA, USA conference of the SPIE- The International Society for Optical Engineers, (*Optical and Photonic Applications of Electroactive and Conducting Polymers*).

The field of CPs has within the last decade seen a very rapid expansion and diversification. Due to this large expansion, R&D efforts worldwide have brought together a very wide variety of researchers from very diverse fields, ranging from materials scientists, physicists, and environmental researchers, to medical/-pharmacological researchers and battery scientists.

Indeed, the titles and subjects in the PART II: APPLICATIONS section of this book - *Batteries, Light Emitting Diodes, Sensors, E/O Devices, Microwave Attenuation, Electrochromics, Anti-Corrosion, Electromechanical Actuators, Lithography, Catalysis, Drug Delivery, Membranes-* speak for themselves in this respect. They show the astoundingly wide applications of these unique polymers.

While there are several extant texts in the field of Conducting Polymers, nearly all are "Editor/Contributor" texts, of a very high level and specialized nature, addressing narrow subfields. They primarily present ongoing research in the contributors' laboratories. These texts oftentimes plunge directly into the thick of high level Conducting Polymer research, without any instruction, or even an explanation of terminology, for the novice or new researcher. They are thus sometimes quite difficult to follow for persons in other areas of the CP field.

The present book seeks to fill this gap. It emphasizes a practical, "how-to" approach, and is written in such a way that a new researcher can instructionally use only the parts relevant to his/her present research. Its target audience includes active researchers in a range of fields in which CPs find application today - for example, a polymer chemist working with composites, a physicist working with NLO (nonlinear optical) materials, a materials scientist working with stealth and radar signature reduction, or a medical or pharmaceutical researcher working with drug delivery -

all of whom need an introductory text to familiarize them with the fundamental aspects of CPs and give them a quick foundation. It also targets students, at the advanced undergraduate or graduate level, and could be included as part of comprehensive instruction in polymer chemistry/physics and materials science. The book is written at a very basic level, and includes problems and exercises.

The author wishes to acknowledge the able assistance of Jennifer Jones, Dorothea Cloughley and several others in the patient editing of this text.

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