
PEDOT

**Principles and Applications of
an Intrinsically Conductive Polymer**

**Andreas Elschner
Stephan Kirchmeyer
Wilfried Lövenich
Udo Merker
Knud Reuter**



CRC Press
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Foreword

After the discovery of electrically conducting polymers in 1977 by Professors Heeger, MacDiarmid, and Shirakawa (Nobel Prize in Chemistry 2000), and more than 30 years of worldwide intense research and huge efforts, PEDOT, or poly(3,4-ethylenedioxythiophene), sets various standards for the entire field. PEDOT, which was invented in 1988 by Bayer AG, Leverkusen, is probably the best conducting polymer available in terms of conductivity, processability, and stability. Furthermore, PEDOT is the only conducting polymer that is commercially produced on a large-scale (nowadays mainly by H.C. Starck Clevios GmbH, Leverkusen) and sold for many applications.

H.C. Starck Clevios GmbH and its predecessors (Bayer AG and H.C. Starck GmbH) in a consequent manner advanced PEDOT to the highly developed commercial product that is presently available in various formulations and conductivities adapted to the needs and specific industrial applications of the customer. The scientists at H.C. Starck Clevios succeeded in making an originally inherently insoluble polymer processable, mostly as dispersion, by optimizing monomers, polymerization route, composition of the dispersion, counteranions, and by secondary doping.

The text covers all relevant aspects of PEDOT beginning with a historical view on conducting polymers and polythiophenes, in particular. The story continues by describing the invention of PEDOT based on the development of the suitable monomer EDOT and subsequent important polymerization routes to the conducting polymer. The properties of PEDOT depend on counterions, which led to the development of PEDOT:PSS, or poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), dispersions, which is the basic form of the commercial product. In the second part of the book, important applications in electronics and organic electronics concomitant with technical and commercial aspects are extensively described.

This comprehensive book about PEDOT, written by experts from H.C. Starck Clevios GmbH, Leverkusen, will represent an indisputable and valuable source for researchers, developers, and users of PEDOT. I wish the book great success.

Peter Bäuerle

Preface

In 2000, the Nobel Prize for Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa “for their discovery and development of conducting polymers” (as written on their Nobel Prize diploma). This prize not only appreciated the scientific work of the Nobel Laureates and the universal importance of their research; a new class of chemical compounds, not broadly known by the public before, came into the limelight. Since then, the conductive polymers have won growing attention in the scientific world, and the public now has more benefits from innovations due to the increasing technical usage of conductive polymers.

Poly(3,4-ethylenedioxythiophene), abbreviated PEDOT or PEDT, belongs to the nevertheless moderate amount of conductive polymers, which have not only attracted remarkable scientific interest but also serve as technically used materials in different products of modern life.

The story of this book started several years ago with a lecture during the π 5 Conference in Ulm/Neu-Ulm (Germany) at the 5th International Symposium on Functional π -Electron Systems. S.K. was invited to hold a plenary lecture about PEDOT from the industrial point of view or, more precisely, from the standpoint of a PEDOT manufacturer. In this situation, the lecturer had to bring together the presentation of fundamental scientific investigations and the description of a technical product with advantageous properties covering not only the facts, but also a little “technical forecast.”

This seemed to have been fulfilled rather successfully, as the demand for more information about PEDOT steadily grew within the scientific community during the years that followed. The authors were repeatedly asked for further lectures, reviews, and book chapters about PEDOT. The growing commercial product paralleled a growing need for easily available and concise, yet comprehensive publications.

When CRC Press invited us to write an entire book about PEDOT, we were initially not too excited by the suggestion. Refusing this kind invitation was a seriously discussed topic. PEDOT was the focus for all of us: Producing commercial quantities of PEDOT; serving customers; investigating PEDOT chemistry and physics, especially in PEDOT-based devices; writing patent applications regarding new PEDOT-relating inventions; publishing full or preliminary papers, giving conference lectures about PEDOT; and so on. PEDOT was a full-time job for all of us, without the added task of writing a book. On the other hand, PEDOT is, roughly speaking, only one chemical and known for only about two decades. How could one fill more than 250 book pages with information a reader would be interested in? Could there be enough material worth a deeper discussion in a book?

Most arguments against this project were extinguished as we looked at the number of PEDOT patents and scientific papers published every year. Between 1989 and 2005, these numbers nearly followed a steadily increasing exponential function, every year exceeding the numbers of the last one. Since then, a slight slowing occurred. Yet at its high level of more than 1000 documents, every year outnumbered the previous year by 10% or more until 2008. And for 2008–2009, the last years with complete figures, an approximately constant value of about 1500 documents per year was reached. It was obvious that a remarkable interest in PEDOT within the scientific community exists, and since about 40% of these figures represent patent applications, an additional intense industrial interest in PEDOT was also demonstrated. Meanwhile, a three-digit number of companies had generated inventions utilizing PEDOT, a persuasive fact symbolizing the industrial success of PEDOT.

When the first conductive polymers were created, technical applications were soon discussed, but a big commercial success was not foreseeable. When PEDOT was invented in 1988, not a single technical application for conductive polymers existed or, to be more precise, no realized application existed although a huge number of potential applications had been announced. Since then this has changed dramatically, to a large extent due to various utilizations of PEDOT. Several other highly conductive polymers, known even earlier than PEDOT, were also introduced into the market and have found some technical usage, such as polyaniline and polypyrrole. But PEDOT still remains *the* preeminent example because of its very pale color and high transparency in combination with its high conductivity and stability.

Another important point is that PEDOT has stimulated basic scientific research in many fields. Improvements and progress in the fields of, for instance, light-emissive display or semiconductor research, were substantially facilitated by the incorporation of PEDOT layers into the devices.

So, after some pros and cons, we dared to write this book. The concept of the book is to meet the requirements of readers from different directions. Great emphasis has been presented on the technical usage of PEDOT. We try to demonstrate the enormous and steadily growing applicatory relevance of PEDOT. Much space is dedicated to the applications of PEDOT including the chemical and physical background for technical utilization. If we can inform the reader about the numerous and distinct technical products containing PEDOT, an important goal of this book will have been met. In other words, explaining the chemistry behind, as far it concerns the conductive polymer PEDOT, cellular phones, LED lamps, and other chemical products is one objective of this book.

Another intention of the book is to provide broad information about the chemistry and physics of PEDOT. There has been a vast amount of interesting new chemistry with EDOT, PEDOT, and its derivatives that has been published in the last 20 years, only to some extent covered by comprehensive reviews until now. Perhaps specialists in the field of conductive polymers will not need the repetition of extremely detailed information, but it

is hoped that they too will appreciate the compilation now available in one book. But with the goal to meet the expectations of specialists, we added several unpublished results from our work and also included a lot of information from patents, which are sometimes not intensely taken into consideration in scientific papers. Therefore, we often tried not to go into too much detail and provided enough references for further study for chemists and physicists who have only marginally engaged in conductive polymers. We apologize to all scientists active in (P)EDOT chemistry who may miss major contributions: Several thousand (P)EDOT publications were checked by the authors, and assessment or even locating the most important ones may have been inaccurate due to the huge number of scientific papers and patents, and the human factor.

Last but not least, the historical development of conductive polymers from laboratory curiosities of unknown structures to small-scale chemicals of paramount scientific importance to multiton commercial technical products will be presented. Only a few publications until now have dealt with the science history of conductive polymers, and often only parts of the story have been told. The viewpoint of an industrial research group with the background of more than 25 years of continuous conductive polymer research will be incorporated into the historical description, it is hoped, without expanding this part of the book and ending at the time when PEDOT was commercialized.

The reader will find that this book is not as complete as a handbook, not always as detailed as a specialized review, not always as up-to-date as a rapid communication, not always as scientifically deep as a peer-reviewed full paper, and not always as readable as a popular science (for instance, history of science) article. But the book tries to combine all these aspects for PEDOT, with additional input of formerly unpublished results and personal opinions from the authors. We hope the readers will enjoy this book as much as we enjoy PEDOT chemistry and physics.

Acknowledgments

This book is based on extensive work performed both within and outside the authors' company, H.C. Starck. Of course, without the fundamental discovery of highly conductive doped polyacetylene nothing would have happened. But it was the merit of Jürgen Hocker to start a Conductive Polymer Project within Bayer AG, at that time a rather ambitious project for an industrial company. It is not typical for a profit-oriented global player, busy in nearly every field of industrial chemistry, to fund such a basic research project in the long-term. Here, the vision of Rolf Dhein to believe in the future of conductive polymers on an industrial scale was decisive for overcoming a lot of years without any commercial success. Friedrich Jonas and Gerhard Heywang invented PEDOT after seven years of conductive polymer research within Bayer AG, and this innovative breakthrough cannot be appreciated enough. The complete work in the industrial and the scientific world with PEDOT is based on this innovation and unthinkable without it. Jürgen Heinze was the first researcher outside Bayer AG to recognize the enormous scientific potential of the PEDOT invention, and his contributions were a strong support for the further development in the initial years.

This book would not have been possible without the encouragement of Jill Jurgensen and Allison Shatkin from Taylor & Francis/CRC Press, and their patience with the authors. The management of the authors' company, particularly Gerhard Gille (H.C. Starck GmbH) and Aloys Eiling (H.C. Starck Clevios GmbH), accepted and supported the work of their employees, which had to be done in addition to the day-to-day business—not self-evident in this era of economic challenges. Thanks also to Sonja Raida and Aynur Cansay of our company, who transformed the figures into an acceptable shape. Last but not least, the scientific and professional contributions of Friedrich Jonas, Matthias Intelmann (H.C. Starck Clevios GmbH), and Peter Bäuerle (University of Ulm) and their continuous discussions are highly appreciated.

Authors

Andreas Elschner, Ph.D., was educated as a solid-state physicist at the University of Marburg (Germany) where he received his Ph.D. in 1988. Following a postdoctoral year at Stanford University (California) he joined Bayer AG in 1990, and has been with H.C. Starck since 2002. Dr. Elschner's research focus is on organic electronics and he is responsible for testing and characterizing organic devices and conducting polymers.

Stephan Kirchmeyer, Ph.D., studied chemistry from 1978 to 1984 at the University of Hamburg (Germany) and at the University of Southern California in Los Angeles. Until 2001, Dr. Kirchmeyer worked as a researcher for IBM and Bayer AG. In 2002, he joined H.C. Starck GmbH and since then has held several responsible positions for H.C. Starck's business with conductive polymers and electronic materials.

Wilfried Lövenich, Ph.D., received his diploma in chemistry from the Technical University of Aachen (Germany). He then went to the University of Durham, Great Britain, to obtain his Ph.D. In 2002, Dr. Lövenich joined H.C. Starck, working as an R&D chemist on the development and pilot plant production of the conductive polymer PEDOT. Since 2009, Dr. Lövenich has been the head of the R&D group of H.C. Starck Clevios GmbH.

Udo Merker, Ph.D., studied physics at the University of Bonn (Germany) from 1989 to 1994. He received his Ph.D. in 1998 for studies in molecular spectroscopy at the University of Bonn and Princeton University (New Jersey). From 1998 to 1999, Dr. Merker was a postdoctorate at the Chemistry Department of Princeton University. In 1999, he joined the corporate research division of Bayer AG to work on the development of electronic materials. From 2002 until 2008, Dr. Merker was responsible for the development of new materials and processes for electrolytic capacitors in the central R&D division of H.C. Starck GmbH. Since 2009, he has been the head of the application technology group of H.C. Starck Clevios GmbH.

Knud Reuter, Ph.D., studied chemistry from 1969 to 1974 at the University of Dortmund (Germany) where he received his doctoral degree with a thesis in organometallic chemistry in 1977. In the same year, Dr. Reuter started his professional work as a member of a polymer research group at Bayer AG. Since 2000, he has worked on PEDOT chemistry, joining H.C. Starck GmbH in 2002.

Abbreviations

AFM	Atomic force microscopy
DMF	N,N-Dimethylformamide
DMSO	Dimethyl sulfoxide
EDOT	3,4-Ethylenedioxythiophene
EPR	Electron paramagnetic resonance
ESR	Equivalent series resistance
GPE	Guest polyelectrolyte
HPE	Host polyelectrolyte
MDOT	3,4-Methylenedioxythiophene
$\mu\text{C/g}$	Microcoulomb/gram
NMP	N-Methyl-2-pyrrolidone
Ohm/sq	Ohm/square
Ω/sq	Ohm/square
PEC	Polyelectrolyte complex
PEDOT	Poly(3,4-ethylenedioxythiophene)
ProDOT	3,4-Propylenedioxythiophene
PSS	Polystyrenesulfonic acid
SEM	Scanning electron microscopy
STM	Scanning tunnel microscopy
S/cm	Siemens/centimeter
TCNQ	Tetracyanoquinodimethane
THF	Tetrahydrofuran
UPS	Ultraviolet photoelectron spectroscopy
VRH	Variable range hopping
XRD	X-ray diffraction

1

The Discovery and Development of Conducting Polymers

1.1 The Scope of This Historical Overview

A lot of fragments of the conducting polymers scientific history can be found in the chemical literature or in Internet articles. There are several specialized chapters in monographs, and also remarks in publications, dealing with early investigations in the special field of the respective paper, including a more or less adequate number of citations. Also anecdotes, dealing with the influence of the human factor in the history of conductive polymers can be found, particularly on the Internet.

The following chapter tries to give an overview from the perception of the authors. A sufficient compromise between details, completeness, understandability for nonspecialists, and novelty for specialists is not easy to find. Furthermore, historical aspects can be a matter of subjective assessments. As a result, a combination of hard facts and information on one side mixed with personal opinion, and older information, replenished by more recent developments, will be presented. To be readable for nonspecialists of conductive polymer chemistry and to give references to more detailed information for interested readers are further goals.

As this book is a PEDOT, or poly(3,4-ethylenedioxythiophene), monograph and PEDOT is one of the most highly conductive polymers, the historical overview focuses on highly conductive polymers directly competing with PEDOT. Hence, this chapter is not extended to all π -conjugated polymers, as it is often found in reviews in this field. A short overview of polythiophenes other than PEDOT—mainly to be classified as semiconductors—will be given in Chapter 3, where the development of PEDOT is described in the context of thiophene chemistry.

Last but not least the chapter follows the wonderful advice cited by W. James Feast in his contribution “Synthesis of Conducting Polymers” in the second edition of the *Handbook of Conducting Polymers*, although not used in the very same sense¹:

"Where shall I begin, your Majesty?" he asked. "Begin at the beginning," the King said, gravely, "and go on till you come to the end: then stop."

—Lewis Carroll,
Alice's Adventures in Wonderland

So the historical overview will begin—after the inevitable introduction—at the true beginning.

1.2 Introduction

What is a polymer? This was a controversial question just before synthetic polymers were prepared for the first time, not to speak of "conducting polymers." The character of macromolecules was the topic of fundamental discussions in the first half of the 20th century—one of the most fascinating scientific debates in the history of chemistry. After Hermann Staudinger's concept of covalent bonds between the building blocks of macromolecules was accepted by the scientific community, the tremendous scientific and industrial development of synthetic polymers got a new and even more expansive dimension.

The Internet allows a quick and easy answer to the question, What is a polymer?

A naturally occurring or synthetic compound consisting of large molecules made up of a linked series of repeated simple monomers. (*The Free Dictionary*, Farlex, July 2010)

A polymer is a substance composed of molecules with a large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds. (Wikipedia, The Free Encyclopedia, September 30, 2007)

To give a clear and precise definition of the term *polymer* is the intention of IUPAC: "A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass."

On a second glimpse, this definition lacks a little bit from clarity, because *high*, *low*, and *multiple* are not very well defined. We will see in the course of this book that several conductive polymers are not really "poly"mers. Nevertheless, they have been attributed as "the 4th generation of polymeric materials," clearly demonstrating the enormous importance of this class of chemical compounds.²⁻⁴

Besides the problems of clearly defining a polymer, the complete term *conducting polymer* also can be misunderstood, because it is used with two

different meanings in the scientific literature. The blends of electrically conductive additives, like metallic fibers or carbon in its graphite modification, with duromers or thermoplastic polymers sometimes are denoted conductive polymers.^{1,5} Often they are called *extrinsically conductive polymers*. Because the polymer itself behaves as an insulator, this can be misleading. The term *conductive polymers* used in this book deals only with *intrinsically conductive polymers* (ICPs).

Conductivity borderlines between electrically isolating, semiconducting, and conductive materials are fluent and not precisely defined. An overview with typical, widely accepted ranges of conductivity for these three, not very sharply separated material classes is given in Figure 1.1.

Conjugated polymers and their conductivity obtainable today are inserted into Figure 1.1. The conductivity range of these polymers has been extended widely in the last few decades. It is obvious that adjusting the desired (particularly this means medium to high) conductivity for a polymeric material is a very difficult challenge; some sort of “molecular engineering” is required. This chapter describes the intriguing story of how this challenge has been met in the last 150 years, starting with the first tentative experiments without

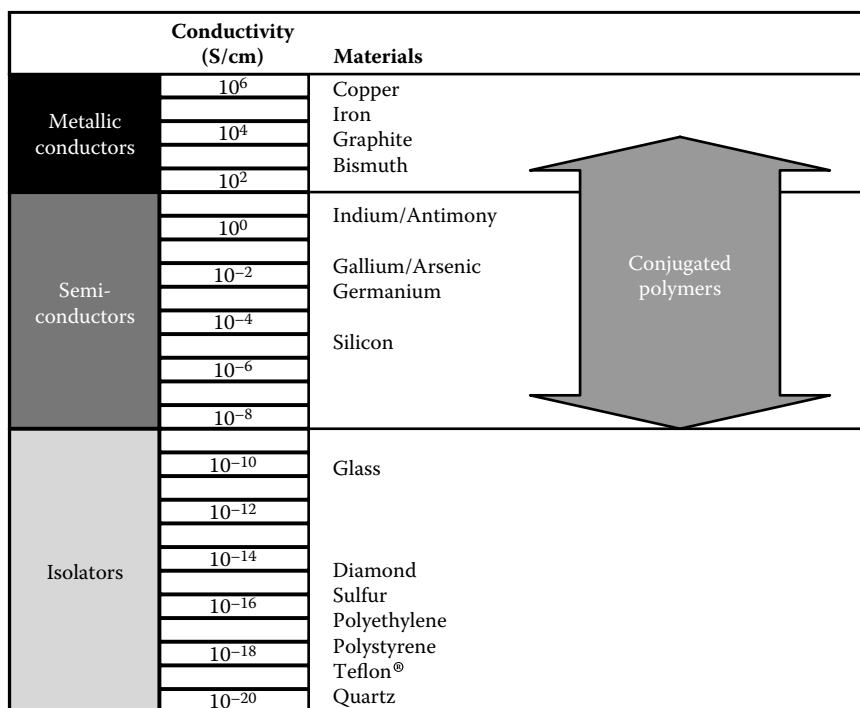


FIGURE 1.1

Electric conductivity of isolators, semiconductors, and conductive materials.

a defined goal in material properties to more systematic chemical syntheses and at the end to real technical breakthroughs in the last quarter of the 20th century. It is not possible to present an exhaustive survey over the vast amount of original literature dealing with all types of conductive polymers. But a first access for readers particularly interested in the historical development is given, and more details of the actual developments should be traceable by the references and the following chapters.

The topic of this book, poly(3,4-ethylenedioxythiophene), abbreviated PEDT or, more common, PEDOT, is regarded as one of the highlights, placed at the end of this short history. The huge number of scientific PEDOT publications and patents (more than 1000 per annum), the large quantities of PEDOT-derived products commercially sold every year and the remarkable impact of PEDOT on daily-life goods show the importance of PEDOT as an ICP. Of course, there have been many other ICPs in the past, culminating in the Nobel Prize dedicated to conductive polymer chemistry in 2000. PEDOT:PSS, or poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), was already mentioned as a prominent example in the Advanced Information of the Nobel Committee for Chemistry and the Royal Swedish Academy of Sciences regarding the year 2000 prize.

1.3 An Early Example: Polyaniline

One of the most important moments in the discovery and investigation of conducting polymers was the publication of the doped polyacetylene in 1977.^{6,7} The fundamental discovery of the simplest organic conjugated hydrocarbon $(CH)_x$, combined with its enormous conductivity obtained by “doping” with, for instance, halogens, was honored by the Nobel Prize in 2000.^{3,4,8–11} The Nobel Laureates—Alan J. Heeger, Hideki Shirakawa, and Alan G. MacDiarmid—initiated a tremendous development in 1977, leading to a huge and steadily growing number of scientific publications, promising technical results, and even various commercial industrial uses.

But the conductive polymer story in its widest sense apparently started as early as 1862, when H. Letheby, a chemistry professor at the College of the London Hospital, tried to check the behavior and selected chemical reactions of aniline. He was motivated by two cases of fatal poisoning by nitrobenzene, where aniline had been found as a metabolite in the stomach of the victims.¹²

Letheby electropolymerized aniline sulfate to a bluish-black solid layer on a platinum electrode and published his results in the *Journal of the Chemical Society*.¹² The chemical nature of the colored, aniline-derived layer essentially remained more or less unknown at that time. The same is true for several

colored products, which were also described in Letheby's paper, obtained by the reaction of aniline with different chemical oxidants. A brilliant bluish-green oxidation product of aniline (later called emeraldine) had been first described as early as 1834 by F. F. Runge.¹³ It is not easy to track the complete literature from those early days, but the chemical oxidation of aniline to intensely colored, nearly black pigments was checked also by J. Lightfoot around 1860. He utilized aniline black for dyeing textiles or printing on fabrics in a U.S. Patent in 1863¹⁴ (perhaps based on experiments dating from 1859).¹⁵ After some technical adjustments, aniline black was then used in the 19th century in a large-scale for textile printing and dyeing.¹⁵ An intriguing marginal note shall not be omitted:¹⁵ When the young William Henry Perkin in 1856 oxidized toluidine-contaminated aniline with potassium dichromate, he found mauvein, the famous first synthetic dyestuff. The byproduct besides the purple mauvein, is separated as the undesirable residue after alcohol extraction and isolation of the mauvein and discarded, obviously was a (toluidine modified) aniline black, considered useless!

Letheby's publication—the actual birthday of polyaniline and an early landmark in electropolymerization, although its potential remained unidentified at that time—was frequently ignored by more recent papers. More than 100 years later another, possibly fundamental investigation that did not receive much attention was published during the dawn of conducting polymers out of the medical scene. A paper by McGinness, Corry, and Proctor of the University of Texas Cancer Center in *Science* dealt with the biological pigment melanin, isolated from human tumor material, and its tunable electric conductivity.^{16,17} A closer look at this macromolecule (Figure 1.2) shows that it is indeed combining structural moieties of (oxidized) aniline and polyacetylene in its expanded conjugated π -system (biologically formed from an indole precursor).

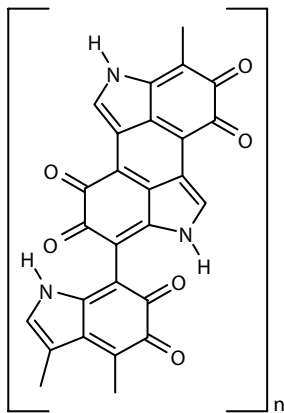


FIGURE 1.2
Simplified structure of melanin.

The response from the scientific community seemed to be very unsatisfactory for the authors, as traceable by the frustrated debate after the Nobel Prize decision in the year 2000.¹⁸ In a few words: Both publications with medical background remained “curiosities,” only moderately recognized. Right?

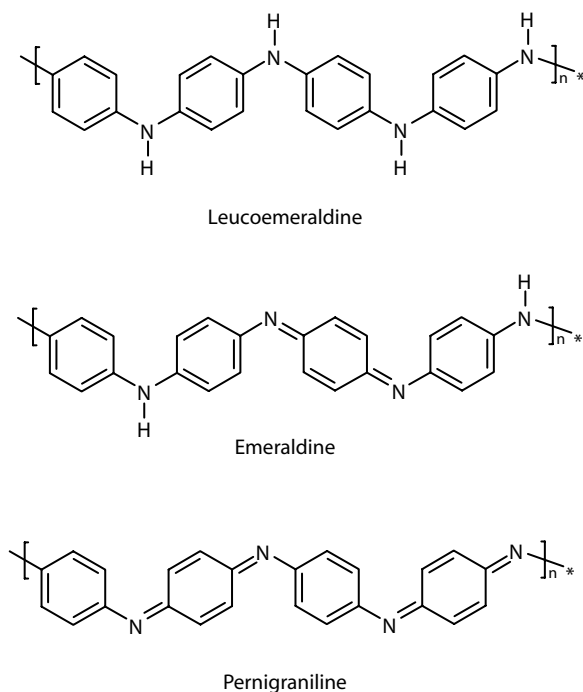
To complete the exciting polyaniline story, we have to go back to the 19th century and to the early experiments. New results in polyaniline research after Letheby's first investigations only sporadically turned up in the scientific literature. In 1891 Goppelsroeder published polyaniline (“aniline black”) again in an illustrated special issue of the German *Elektrotechnische Rundschau* (*Electrotechnical Review*).¹⁹ Goppelsroeder used the electrolytic oxidation of “aniline chloro hydrate” to aniline black for writing, as demonstrated by a picture from 1891.¹⁹ In his own words, Goppelsroeder performed “electrochemical writing or painting.”

Several other publications appeared around the turn of the century, sometimes in less common journals (see Liechti and Suida,²⁰ Dobroserdoff,²¹ Grandmougin,²² Böttinger and Petzold,²³ and Nover²⁴), and with some erroneous chemical interpretations. They do not need to be discussed here in detail. The mistakes are excused by the complicated chemistry and the state of analytical methods at that time.

A deeper knowledge of polyaniline evolved between 1907 and 1911, when future Nobel Laureate Richard Willstätter in his typical, strictly methodic way of research, characterized the oligomeric oxidation products of aniline.^{25–28} Starting only a short time later Arthur G. Green et al. at the Department of Tinctorial Chemistry of the University of Leeds also studied polyaniline and completed, corrected, and reinterpreted Willstätter's results.^{29,30} Willstätter replied controversially,³¹ and Green answered once more³²—a rather typical scientific dispute in those days.

The names for completely oxidized aniline black (pernigraniline), for the pale reduced form of polyaniline (leucoemeraldine), and for the green, half-oxidized intermediate (emeraldine), and their assignment to chemical structures were finally confirmed. At the end of these discussions some well-founded knowledge about polyaniline had been achieved, and the formulae presented by Green were accepted and established in the scientific literature. It should be noted that in this time the macromolecular character of polyaniline or aniline black was not recognized. For all these products, defined monodisperse oligomers with 8 aniline moieties ($n = 2$ in Figure 1.3) were formulated. Leucoemeraldine, emeraldine, and pernigraniline as the three most important oxidation states of polyaniline were drawn in popular textbooks (for example, see Beyer³³ and Fieser and Fieser³⁴) in the 1960s as depicted in Figure 1.3 ($n = 2$).

A more detailed overview with all five oxidation states to be formulated for oligomeric ($n = 2$) polyanilines is given by Groenendaal et al.³⁵ The concept of defined octamers was used until the early 1970s, when polyaniline for the first time came into the focus of the chemical industry due to its (semi)conducting properties, for example, in Eastman Kodak patents.^{36,37} But this is in anticipation of the subsequent seminal and dramatic changes. Industrially, aniline

**FIGURE 1.3**

Polyaniline oxidation states (free bases only).

black remained to a large extent an affordable and light-fast pigment (for cotton, silk, and synthetic fibers like polyesters) and is used to date for textile printing. Other applications are dyeing of lacquers, plastics, or paper.^{38,39} A closer look from the viewpoint of a dyestuff chemist must include subsequent reactions of emeraldine—condensations and oxidations—to phenazine dyes of technical relevance as the structurally modified top grades of aniline black.³⁸ Since the Lightfoot patent of 1863, the industrial use and scientific interest regarding polyaniline were mainly concentrated on dyestuff chemistry and applications. From a scientific point of view this changed dramatically in the late 1960s when polyaniline was recognized as an electrically conducting organic material.

All compounds depicted in Figure 1.3 with their more or less defined structures are electric insulators. A real progress on the way to highly conductive organic compounds was achieved, when polyaniline and in particular its salts were studied with more emphasis on its unusual electric properties in France.

It was mainly the work of Marcel Jozefowicz and his group in Paris that clearly demonstrated the electronic conductivity of polyaniline salts more than 40 years ago. In several papers polyaniline was presented as a conductive polymer, with the conductivity dependent from the protic doping status. From the paper "Conductivité Electronique et Propriétés Chimiques

de Polyanilines Oligomères” the following passage in the abstract may be quoted as particularly illustrative:

Conductivity results obtained on an emeraldine complex class (sulfates) indicate a reproducible electronic conductivity. The conductivity varies with the hydration and acid-base parameters of different derivatives; its value is very high for an organic material and ranges from 10 to 10^{-4} $\text{ohm}^{-1} \text{cm}^{-1}$ depending on the values of the parameters indicated.⁴⁰

Although the moisture dependence is significant, a remarkable electronic conductivity was found to remain in completely dried samples of emeraldine sulfate.

A lot of papers were published by the Jozefowicz group on conductive polyaniline,^{40–48} including an early review⁴⁹ and first suggestions for technical applications.⁵⁰ But the experimental findings presented to the public “did not give rise to great excitement at that time,” as György Inzelt comments, a little bit amused, in 2008 in his book *Conducting Polymers: A New Era in Electrochemistry*.⁵¹ When R. Buve, who coauthored several Jozefowicz papers, gave a lecture at the 18th meeting of CITCE at Elmau in 1967, he had to reply to only two questions in the discussion, as can be traced by the published version in *Electrochimica Acta*.^{45,51} Although relevant and of technical interest, the questions did not disclose that the audience realized the true scientific breakthrough behind the new results with polyaniline, and the same seems to be true for the scientific community of those days.

In the same era of the 1960s, work from Czechoslovak researchers established the concept of iodine doping for polyaniline. A conductivity of up to 1 S/cm for polyaniline–iodine complexes was obtained.⁵²

In 1974, a few years before the spectacular progress for polyacetylene was published, the electronic conductivity of polyaniline was confirmed again in an interesting paper by investigations parallel with another conductive polymer, which had become known in the meanwhile as polypyrrole (see Section 1.4). A remarkable specific conductivity in the range of 5 to 30 S/cm was achieved.⁵³

Surprisingly, the aforementioned basic work was disregarded later with the phrase “a few scattered papers by other groups.”⁵⁴ MacDiarmid, Epstein, and their colleagues reinvestigated polyaniline in the 1980s, and broadly extended the knowledge about it and remarkably increased the achievable conductivity of PANi (published in many fundamental papers⁵⁵; easily traceable in several comprehensive articles and reviews).^{54,56,57} Consequently, the industrial use of conductive polyaniline marked the successful end of a long development, actual suppliers being Ormecon GmbH^{58,59} in Germany and Panipol Oy⁶⁰ in Finland. However, the intense color of polyaniline can be a serious drawback in technical applications, when transparency in the visible range of the spectrum and a pale color is required.^{61,62} So, preferred applications are conductive blends (extrinsically conductive polymers) with thermoplastic resins^{60,63–65} and active additive in corrosion primers.⁶⁶

1.4 The First Electrically Conductive Poly(Heterocycle): Polypyrrole

Not as early as polyaniline itself, described first in the 19th century, but shortly before the discovery of polyaniline conductivity, another interesting group of electrically conducting polymers emerged. The polypyrroles appeared in this field as the first example for conductive poly(heterocycles). From the early 1960s, marked by the work of D. E. Weiss, B. A. Bolto, and coauthors in Australia, until today, the polypyrroles remained one of the most interesting groups of conducting polymers, also with respect to having potential applications.

In a series of publications in 1963, Weiss et al. described the thermolysis of 2,3,4,5-tetraiodopyrrole to macromolecular networks.^{67–69}

These polypyrroles exhibit an electric conductivity depending on the degree of doping by iodine, as symbolized by the nonstoichiometric equation in Figure 1.4. The term *doping* was not used by the authors for the charge transfer complexes between the polypyrrole network and iodine eliminated from the heterocycle. As the result of the polyfunctional starting material, the polypyrrole of the Australian researchers could not exhibit the essentially linear structure of polypyrroles developed later on by other workgroups. A specific conductivity of about 1 S/cm was achieved.

In 1968/1969 Dall'Olio et al. in Parma, Italy, revitalized polypyrrole chemistry by oxidizing pyrrole itself electrolytically to pyrrole black ("noir d'oxypyrrol").⁷⁰ In contrast to the investigations of Weiss et al., Dall'Olio and his coauthors focused on the electrochemical behavior of pyrrole and its electropolymerization. The paramagnetic behavior of the polymer was studied (the g-factor of the free radical was measured to 2.0026 by electron spin resonance spectroscopy), and a remarkable electric conductivity of 7.54 S/cm at ambient temperature was found.

About 10 years later, industrial research activities at the IBM Research Laboratories (San Jose, California) again demonstrated the high conductivity of electrolytically deposited polypyrrole films.^{71,72} A period of broad investigations followed, traceable, for instance, in the first edition of the *Handbook of Conducting Polymers* in two polypyrrole chapters.^{73,74}

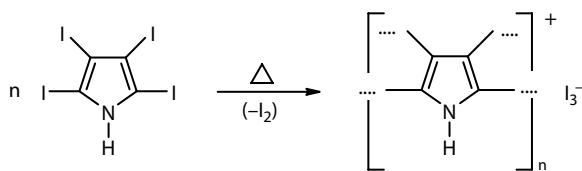


FIGURE 1.4

Conductive, doped polypyrrole network from tetraiodopyrrole.

The technical development of the polypyrrole led to several applications. Actually, the electrochemical polymerization is used in tantalum capacitors by Sanyo Electric Co.⁷⁵ and in aluminum capacitors by Panasonic.⁷⁶

The Dutch company DSM has commercialized polypyrrole as a prefabricated polymer in the form of a core-shell system with a polypyrrole outer layer and a core of mica or polyurethane particles (ConQuest®). These products are, as to the best knowledge of the authors, no longer available by DSM.

1.5 The Fundamental Breakthrough: Doped Polyacetylene

The decisive breakthrough of 1977 by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa has its own history. The experimental work—and the intriguing scientific discussions—culminated in the two seminal publications:

Electrical Conductivity in Doped Polyacetylene, C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Physical Review Letters*, 39(17), 1098–1101 (1977).⁶

Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)_x, H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *Journal of the Chemical Society, Chemical Communications*, 578–580 (1977).⁷

The authors classified their work in the tradition of solid state physics and chemistry: The formerly existing nonmetallic conductors compared to doped polyacetylene by the authors in their texts are, as the example for a highly conductive organic material, single crystals of the charge–transfer complex tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), first described in 1972/1973^{77–79} (see Figure 1.5) and, as the example for a highly conductive polymeric material, the inorganic compound (SN)_x.^{80,81}

A closer look at the scientific way Heeger, MacDiarmid, and Shirakawa went, resulting in the discovery of doped polyacetylene, demonstrates the preeminent role of (SN)_x in the course of this development. A second, very important aspect is the interdisciplinarity and internationality of the work. Third, the role of serendipity in chemical research should not be underestimated; and doped, highly conductive polyacetylene is another example. In so far, polyacetylene (PAC) is in a line with penicillin, x-rays, Teflon, and high density polyethylene (HDPE)—all of them being invented with the aid of accidents; this line can be prolonged without major difficulties.

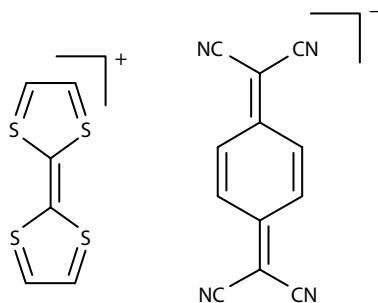


FIGURE 1.5
TTF-TCNQ complex.

Polyacetylene as a chemical individual was observed as early as 1874,^{82,83} when the tendency of acetylene to decompose to untractable solids was first described. Later, photo- or radiochemical methods to form acetylene polymers (or oligomers) were described.⁸⁴ A more practical way to PAc was found and intensely investigated in the 1920 and 1930s. The first examples were the work of Kaufmann and colleagues.^{85,86} As obtained by the catalytic action of cuprous or cupric oxide (Cu_2O or CuO) or by copper in the presence of oxygen, the name *cuprene* for the solid PAc was created. The exact nature of the cuprene materials remained relatively ambiguous because of their unsolubility and hence very difficult analyses.

A synthetic breakthrough in the synthesis of PAc, especially of PAc as a linear high polymer, was achieved by the future Nobel Laureate Giulio Natta in 1958 when he applied Ziegler–Natta catalysts in the polymerization of acetylene for the first time.⁸⁷

As a potentially conductive polymer, polyacetylene was first recognized in 1961 by researchers of the Tokyo Institute of Technology.⁸⁸ Like Giulio Natta, Hatano, et al. polymerized acetylene by Ziegler–Natta catalysts; mixtures of triethylaluminium and titanium tetrachloride or titanium tetra-*n*-butoxide were used. Investigation of the structure and measurements of the electric conductivity were performed. The PAc was suggested to be essentially *trans*-conjugated; the electric conductivity of the greenish-black powder did not exceed the semiconducting range and was in the order of 10^{-5} S/cm in the best cases—the more crystalline, the higher. The temperature dependence of the resistance ρ followed the usual equation of an intrinsic semiconductor:

$$\rho = \rho_0 \exp (\Delta E/2kT)$$

This was the state of the art when the group of Hideki Shirakawa in Tokyo started their work with polyacetylene. The now following first step in the technical revolution regarding the electric conductivity of plastics was decisive, but not very spectacular. The full consequences were not recognized

immediately, and it was done serendipitously. What had happened in the laboratory of Shirakawa? The following description mainly follows the personal reports of the Nobel Prize winners.⁸⁹⁻⁹¹

Acetylene had been polymerized in the Shirakawa group with Ziegler–Natta catalyst $[\text{Ti}(\text{O}^n\text{C}_4\text{H}_9)_4-\text{Al}(\text{C}_2\text{H}_5)_3]$ as usual, and of course intractable black-brown powdery solids had been precipitated. Shirakawa was interested in the influence of different catalyst concentrations on the properties of polyacetylene. When a new, visiting foreign student attended the laboratory, Shirakawa advised him to check millimolar concentrations of the catalyst. It is not totally clear afterward what kind of mistake then took place: a language misunderstanding, or a missing letter *m* in the written instructions of Shirakawa, or a misreading of these instructions. Anyway, as the result of the misunderstanding, the student applied molar instead of millimolar concentrations of the two components of the Ziegler–Natta catalyst.⁸⁹⁻⁹²

The appearance of the polyacetylene product dramatically changed. Instead of being unsightly dark brown, the PAc obtained consisted of silvery lumps. In spite of this metallic look, the conductivity of the new modification of PAc was not significantly enhanced, but the material was far better processable into films, which were accessible for spectroscopic investigations and so forth. Several interesting papers published by the Shirakawa group described the synthesis and properties of this special new polyacetylene with metallic luster that could elucidate a lot of structural features.⁹³⁻⁹⁶ But until the mid-1970s, nothing else happened. Despite the progress Shirakawa had achieved, polyacetylene continued as a laboratory curiosity. The electric conductivity was not thrilling, especially compared to the conductive organic polymers already known, polyaniline and polypyrrole, which showed up to about five orders of magnitude higher conductivities.

Nevertheless, and perhaps just therefore, this “1000-fold” experiment was one of the magic moments in chemical history, comparable to several other remarkable breakthroughs in science. But before getting aware of this fact, another scientific group at the opposite end of the world had to play a decisive role, and a second magic moment had to come about.

At the University of Pennsylvania (Penn) in Philadelphia, the physicist professor Alan J. Heeger had a discussion with Alan G. MacDiarmid, a chemistry professor, about the inorganic conductor poly(sulfurnitride) $(\text{SN})_x$, a polymer with a typical golden-metallic luster. Heeger was intrigued by several quasimetallic properties of this novel compound. A fruitful collaboration about $(\text{SN})_x$ was established in the mid-1970s, crossing the chemistry–physics border after some initial “language” problems (confusing Sn, metallic, element tin; and SN, sulfur nitride).^{89-92,97}

When MacDiarmid later—at that time in 1975 he was a visiting professor at Kyoto University in Japan—visited the Tokyo Institute of Technology, he reported about the Heeger and MacDiarmid work on $(\text{SN})_x$. Shirakawa and MacDiarmid met “over a cup of green tea” and showed each other their lustrous samples: golden $(\text{SN})_x$ and the silvery polyacetylene in the form of

shiny films. Both researchers were fascinated by the unusual appearance of $(\text{CH})_x$, since a formally simple hydrocarbon with a metallic appearance had never been seen before. So they decided to get more knowledge about this compound, which was supposed to be perhaps even more remarkable than already known, and to further extend the studies of Shirakawa. Shirakawa was invited to Penn as a visiting scientist.

When the $(\text{CH})_x$ synthesis was repeated in Philadelphia, a rather low conductivity was observed again, in spite of the metallic appearance. The product was not very pure, and so the researchers decided to strictly remove all impurities from the polyacetylene, with the opposite effect than expected: the conductivity decreased. Obviously, small halogen impurities measured by elemental analysis had a positive influence. So, an experiment analog to $(\text{SN})_x$ chemistry, where the addition of bromine is known to increase the conductivity by one order of magnitude, was made.

The effect achieved by addition of bromine was not as moderate as with sulfur nitride but really dramatic. An extremely high conductivity was immediately observed, and the electrometer was destroyed. On this November 23, 1976, a 10-million-times-enhanced conductivity for the so-called doped polyacetylene (Figure 1.6) was obtained—the birthday of the first highly conducting hydrocarbon! The enormous significance of this experimental breakthrough was quickly realized, as traceable by a letter to Kenneth Wynne, the program officer in the U.S. Office of Naval Research responsible for funding the visit of Shirakawa at Penn. With this letter, written by MacDiarmid, a copy of the seminal paper submitted to Chemical Communications was forwarded to Wynne.⁹² A short passage from this letter, demonstrating the enormous relevance attributed to this discovery by their originators, is cited by Hall:

As you will doubtless observe, we believe this is an extremely important and exciting new area and, although we would not say it in public, we have other information which leads us to believe that some of the species are indeed metallic!⁹²

Twenty-three years later, the Nobel Prize in Chemistry was awarded to Heeger, MacDiarmid, and Shirakawa.⁹⁸ Their fundamental research had kicked off a tremendous development, from a scientific point of view as well as in the chemical industry. But all expectations regarding practical,

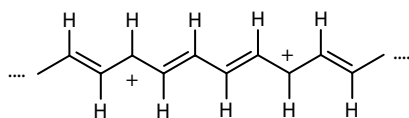


FIGURE 1.6

Polyacetylene in its highly conductive dicationic form (one mesomeric structure).

industrial applications for doped polyacetylene were in vain. The difficult processability and relative instability—measured at long-term standards in technical use—played the pivotal role in this failure.

At the end of the 1980s, vast scientific progress in the field of conducting polymers had been achieved, several applications were suggested, and the world record in electric conductivity for organic materials was set in 1987 with stretched, iodine-doped polyacetylene by Naarmann and Theophilou to about 100,000 S/cm.⁹⁹ Nevertheless, from a technical point of view, the statement of Billingham and Calvert written in 1988 in their article “Electrically Conducting Polymers: A Polymer Science Viewpoint,”¹⁰⁰ was still valid: “If one asks what are the applications of conducting polymers, the short answer is ‘none.’”

In the same review,¹⁰⁰ the (apparently) experimentally well supported opinion of Münstedt is cited:

*That the whole range of common conducting polymers is unstable in accelerated tests of conductivity decay. He suggests that the carbenium ion structures, which are required to permit conduction in conjugated polymers, are incompatible with the presence of oxygen and water and that the only practical route towards conducting polymers which have environmental stability comparable to graphite, will be to seek structures whose band gap is intrinsically small enough to allow thermal excitation without the need for doping.*¹⁰¹

At the end of the 1980s, the technical situation began to change. The aforementioned investigations¹⁰¹ clearly demonstrated insufficient conductivity half-life values of polyacetylene, polypyrrole, polythiophene, polyaniline, and TTF-TCNQ under accelerated testing in humid air or at inert conditions. But the ink used for writing the previous statements had not dried yet, when the invention of PEDOT (the polymer based on 3,4-ethylenedioxythiophene [EDOT], see Figure 1.7) just demonstrated the opposite: doped PEDOT emerged as a highly conducting polymer stable in air up to very high temperatures, to humidity including moist air, also at elevated temperatures, and, after only a few years of further development, even processable in water.

Several fundamental patent applications regarding the utilization of special conducting polymers were filed. In the following 20 years, polyaniline,

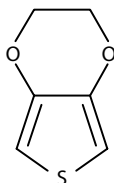


FIGURE 1.7

3,4-Ethylenedioxythiophene (EDOT).

polypyrrole, and special polythiophenes found their way into the market. Some details regarding polythiophenes will be presented later. The most successful and widely used polythiophene, PEDOT, produced and technically applied in steadily growing multiton amounts per year as the only commercialized example for a highly conductive polythiophene, is the focus of this book.

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