

G. Inzelt: Conducting Polymers

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Intrinsically conducting polymers have been around for quite a while. In 1834, Runge reported a black substance obtained by treating aniline with oxidizing compounds. Fritzsche provided a more detailed description of this material as an oxidation product of aniline in 1840. Electrooxidation of aniline was first performed by Letheby in 1862; some improvement of the description (the product was actually an oligomer) was provided 1876 by Gopelsroeder. In 1909, Willstätter and Dorogi provided for the first time the now well-known picture of an aniline chain with head-to-tail coupling (in the para-position of the benzene ring), confirmed 1910 by Green and Woodhead.

The detailed properties of intrinsically conducting polymers have been obtained more recently, starting with a seminal report from the electrochemists¹ point of view by Diaz and Logan in 1980.² Recognition in terms of a Nobel Prize finally arrived in 2000. Thus it appears appropriate to review the state of our knowledge by an expert in this field supplementing numerous reviews published in books, journals and series.

A proper definition of the subject is important. There is good reason to call the materials intrinsically conducting polymers and not just simply—as preferred by the book's author—conducting polymers. Macromolecular substances with all kinds of conducting materials added to confer electric conductance to an initially insulating material have been around for quite some time, and they have been widely used. And there are even materials like (SN)_x. The book title provides a somewhat misleading abbreviation—the book reviewed here deals almost exclusively with

intrinsically conducting polymers (ICPs). Taking into account the authors presumed aim—to provide an update and description of the state-of-the-art—a specific literature review providing an update would have been a good idea in this rapidly growing subject. The number of ten thousand publications on the subject—as mentioned in the text—appears to be a low estimate and calls for a systematic approach.

A classification of electrochemically active polymer follows in chapter 2—but already this title indicates that we are looking at something different from the book's title: Redox polymers (not necessarily electronically conducting), intrinsically conducting polymers ICPs (apparently the true subject of the book), ICPs with additional redox functionalities and copolymers from both latter classes of materials. The number of reports and publications on any one polymer is no reliable indicator of its importance (something which is certainly difficult to measure at all), but it appears arbitrary when polymers like e.g. polyflavins (why the s?) or polymelatonin are deemed worthy of a mention whereas polyindole hardly appears as a footnote (on. p. 37) and is not even mentioned in the index; polyindoline is not mentioned at all. A quick search in the reviewer's own databank yielded 48 reports on polyindole and 4 on polyindoline. In an introductory book aimed at the novice in the field such omissions would be harmless but in a book like the present one it leaves the reader puzzled. The compounds which made it into this chapter (even Nafion[®]

¹ Taking their publications as the starting point of the electrochemists affiliation with ICPs the books subtitle "A New Era in Electrochemistry" appears to be somewhat strange.

² It might be argued that a report by de Surville et al. in 1968 and another by Mohilner et al. in 1962 with the former one already addressing the subject of electronic conductivity are the starting points.

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because it is considered an ion-exchange polymer containing electrostatically bound redox center) are briefly described by providing a structural formula and some details of the synthesis and of observed chemical/electrochemical reactions. Certainly some polymers—like e.g. polythiophene or polyaniline—are simply more popular than others but this does not justify a rather arbitrary treatment. In the case of polythiophene, some rather old figures are used to illustrate relationships between Hammett substituent constants and oxidation potentials or between oxidation potentials of the monomers and their respective polymers. It is not clear why the author did not consult another publication by the same authors providing a much broader picture beyond thiophene. Taking into consideration that the work by Waltman et al. was published in the eighties it is even more surprising that more recent approaches based on the ever-growing toolbox of theoretical chemistry (e.g. semiempirical methods or DFT) are not mentioned—there are certainly enough published examples. A short section is devoted to ICPs with covalently attached or otherwise incorporated redox active groups, an even shorter one to copolymers.

A rather extended chapter describes methods: electrochemical, spectroscopic, spectroelectrochemical and topographic ones. For each of the methods, reviews, extensive chapters in monographs or even whole textbooks are available. Thus this chapter appears to be rather redundant. The chapter lacks a systematic approach. In a list of specific methods, spectroelectrochemistry suddenly appear; subsequently some spectroscopic, microscopic and diffraction methods are collected separately.

Although some details of polymer formation have been treated in the second chapter, both chemical and electrochemical methods of ICP synthesis are treated in chapter 4. This part of the book is a selective collection of cyclic voltammograms, a few results of quartz microbalance measurements and some UV-Vis data. Quite a few of those polymers addressed in the second chapter make a return.

Chapter 5 is labelled rather generally “Thermodynamic Considerations”. It particularly considers membrane properties of the polymer films, i.e. ionic equilibria between the interior and exterior of the ICP. The somewhat unconnected issue of polaron/bipolaron systems is addressed at the end (although these terms are not used).

Based on almost the same (rather limited) set of methods (only one set of infrared data has been added) already employed in chapter 4 redox transformations and associated transport processes are discussed in chapter 6. Ion transport is included but anion effects are absent.

Beyond their fascinating materials properties, ICPs show exciting applications. Most of the applications reported in the open literature are mentioned although rather selective attention is paid (e.g. corrosion inhibition efficiency is described only in qualitative terms).

The book is carefully prepared but quite a few structural formulas appear small. In the chapter on the applications of ICPs, some surprising features can be found: On pages 232 and 235 electrochromism of a high quality film of PEN-BTE (the book does not contain a list of acronyms or symbols and acronyms are also missing almost completely in the index) and of PANI are shown in grey scale rather than colour. The index—an important tool in this kind of publication—is a mixed blessing. The reader searching for a particular polymer may be disappointed—neither via the parent monomer nor via the polymer. A compound index would have been a valuable addition and easily prepared with state-of-the-art word processing software.

It is difficult to recommend the book to a particular readership. For a student looking for an introductory text the price is out of reach, in addition the book is hardly an introductory one. The expert may seek a more detailed source of information. The book may find use as an addition to libraries and laboratories where the subject of ICPs is pursued already.