Conducting Polymers

György Inzelt

Conducting Polymers

A New Era in Electrochemistry

Springer

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Elements consisted at first of certain small and primary Coalitions of minute Particles of matter into Corpuscles very numerous and very like each other. It will not be absurd to conceive, that such primary Clusters may be of far more sorts than three or five; and consequenly, that we need not suppose, that each of the compound Bodies we are treating of, there should be found just three sorts of such primitive Coalitions.

—Robert Boyle: The Sceptical Chymist, Oxford, 1680.

Preface

Conducting polymers have permeated many fields of electrochemical research. Like metals and alloys, inorganic semiconductors, molecular and electrolyte solutions, and inorganic electroactive solids, they comprise a group of compounds and materials with very specific properties; indeed, there is now a research field focusing on the electrochemistry of conducting polymers. Conducting polymers possess similarities from an electrochemical point of view to all of the other compounds and materials mentioned above, making them a highly fascinating research topic. Furthermore, such research has led to numerous new applications, ranging from corrosion protection to analysis. There are a huge number of electrochemical papers on conducting polymers, and a good number of books on this topic too. However, the editor of the present series of *Monographs in Electrochemistry* noted that there was no modern monograph on the market in which the electrochemistry of conducting polymers is treated with the appropriate balance of completeness and selectivity. Such a monograph should be written by an active electrochemist who is experienced in the field of conducting polymers, and who possesses a solid knowledge of the theoretical foundations of electrochemistry. Therefore, I am very happy that György Inzelt from the Eötvös Loránd University in Budapest, Hungary, agreed to write this monograph. I hope that graduate students in electrochemistry, the chemistry and physics of materials, industrial chemists, and researchers at universities and industry alike will find this monograph enjoyable and stimulating, as well as helpful for their work.

March 2008

Fritz Scholz
Editor of the series *Monographs in Electrochemistry*

Contents

Chapter 1
Introduction

Polymers have long been thought of and applied as insulators. Indeed, not so long ago, any electrical conduction in polymers—mostly due to loosely bound ions—was generally regarded as an undesirable phenomenon. Although the ionic conductivity of polymer electrolytes (macromolecular solvents containing low-molar-mass ions) and polyelectrolytes (macromolecules containing ionizable groups) have been widely utilized in electrochemical systems over the last few decades (e.g., in power sources, sensors, and the development of all-solid-state electrochemical devices), the emergence of electronically conducting polymers has resulted in a paradigmatic change in our thinking and has opened up new vistas in chemistry and physics [1].

This story began in the 1970s, when, somewhat surprisingly, a new class of polymers possessing high electronic conductivity (*electronically conducting polymers*) in the partially oxidized (or, less frequently, in the reduced) state was discovered. Three collaborating scientists, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa, played a major role in this breakthrough, and they received the Nobel Prize in Chemistry in 2000 "for the discovery and development of electronically conductive polymers" [2, 4–8].

As in many other cases in the history of science, there were several precursors to this discovery, including theoretical predictions made by physicists and quantum chemists, and different conducting polymers that had already been prepared. For instance, as early as 1862, Henry Letheby prepared polyaniline by the anodic oxidation of aniline, which was conductive and showed electrochromic behavior [9].

Nevertheless, the preparation of this polyacetylene by Shirakawa and coworkers and the discovery of the large increase in its conductivity after "doping" by the group led by MacDiarmid and Heeger actually launched this new field of research.

Electrochemistry has played a significant role in the preparation and characterization of these novel materials. Electrochemical techniques are especially well-suited to the controlled synthesis of these compounds and for the tuning of a well-defined oxidation state.

The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still at the foreground of research activity in electrochemistry. There are at least two major reasons for this intense

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interest. First is the intellectual curiosity of scientists, which focuses on understanding the behavior of these systems, in particular on the mechanism of charge transfer and on charge transport processes that occur during redox reactions of conducting polymeric materials. Second is the wide range of promising applications of these compounds in the fields of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening and corrosion protection, etc.

Many excellent monographs on and reviews of the knowledge accumulated regarding the development of conducting polymers, polymer film electrodes and their applications have been published, e.g., [1, 10–53]. Beside these comprehensive works, surveys of specific groups of polymers [40, 49], methods of characterization [50–54] or areas of application [18, 21, 34, 36–38, 47, 48] have also appeared. These novel materials with interesting and unanticipated properties have attracted workers across the scientific community, including polymer and synthetic chemists [13, 14, 22, 23], material scientists [14, 20, 31, 32], organic chemists [17], analytical chemists [16, 21, 36, 45], as well as theoretical and experimental physicists [8, 31, 32].

After 30 years of research in the field, the fundamental nature of charge propagation is now in general understood; i.e., the transport of electrons can be assumed to occur via an electron exchange reaction (electron hopping) between neighboring redox sites in redox polymers, and by the movement of delocalized electrons through conjugated systems in the case of so-called intrinsically conducting polymers (e.g., polyaniline, polypyrrole). (In fact, several conduction mechanisms, such as variable-range electron hopping and fluctuation-induced tunneling, have been considered.) In almost every case, the charge is also carried by the movement of electroinactive ions during electrolysis; in other words, these materials constitute mixed conductors. Owing to the diversity and complexity of these systems—just consider the chemical changes (dimerization, cross-linking, ion-pair formation, etc.) and polymeric properties (chain and segmental motions, changes in the morphology, slow relaxation) associated with them, the discovery of each new system brings new problems to solve, and much more research is still needed to achieve a detailed understanding of all of the processes related to the dynamic and static properties of various interacting molecules confined in a polymer network.

Although the conductivity of these polymers is an interesting and an utilizable property in itself, their most important feature is the variability of their conductivity, i.e., the ease with which the materials can be reversibly switched between their insulating and conducting forms.

In this work, the topics that are presently of greatest interest in this field, along with those that may be of much interest in the future, are discussed. Some of the most important experiences, existing models and theories are outlined, and the monograph also draws attention to unsolved problems. Some chapters are also devoted to the most typical representatives of this group of materials and the most important techniques used for the characterization of these systems. Last but not least, abundant instances of the applications of conducting polymers are described.

The examples presented and the references recommended herein have been selected from more than ten thousand research papers, with emphasis placed on both classical and recent works. It is hoped that this monograph will be helpful to colleagues—electrochemists and non-electrochemists alike—who are interested in this swiftly developing field of science.

Considering the rapidly increasing number of applications of polymers in electrochemical cells, it can be declared that electrochemistry is currently moving out of the Bronze Age (i.e., typically using metals) and into the era of polymers.

Lecturi salutem!

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Chapter 2
Classification of Electrochemically Active Polymers

Electrochemically active polymers can be classified into several categories based on the mode of charge propagation (note that insulating polymers are not considered here except for those with variable conductivity). The mode of charge propagation is linked to the chemical structure of the polymer. The two main categories are electron-conducting polymers and proton (ion)-conducting polymers. We will focus on electron-conducting polymers here.

We can also distinguish between two main classes of electron-conducting polymers based on the mode of electron transport: redox polymers and electronically conducting polymers.

In this chapter we provide examples of each type of electron-conducting polymers, listing some of the most typical and widely studied of these polymers, as well as several new and interesting representatives of this class of materials. Some sections are also devoted to combinations, such as electronically conducting polymers containing redox functionalities and copolymers. Composites are briefly discussed too.

2.1 Redox Polymers

Redox polymers contain electrostatically and spatially localized redox sites which can be oxidized or reduced, and the electrons are transported by an electron exchange reaction (electron hopping) between neighboring redox sites if the segmental motions enable this. Redox polymers can be divided into several subclasses:

- Polymers that contain covalently attached redox sites, either built into the chain, or as pendant groups; the redox centers are mostly organic or organometallic molecules
- Ion-exchange polymeric systems (polyelectrolytes) where the redox active ions (mostly complex compounds) are held by electrostatic binding.

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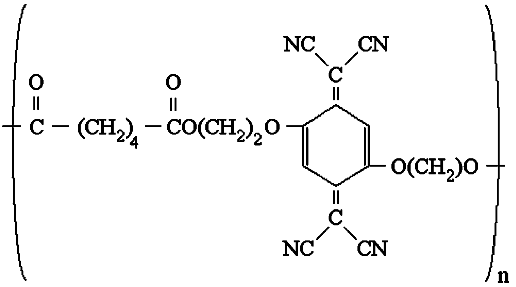
2.1.1 Redox Polymers Where the Redox Group Is Incorporated into the Chain (Condensation Redox Polymers, Organic Redox Polymers)

2.1.1.1 Poly(Tetracyanoquinodimethane) (PTCNQ) [1–21]



Synthesis: 2,5-bis(2-hydroxyethoxy)-7,7′,8,8′-tetracyanoquinodimethane + adipoyl chloride [2, 11].

Redox reaction:

$$\underset{\text{(orange)}}{[\mathrm{TCNQ}]_{\mathrm{polym}}} + \mathrm{e}^- + [\mathrm{K}^+]_{\mathrm{sol}} \rightleftarrows \underset{\text{(blue)}}{[\mathrm{TCNQ}^{\bullet-}\,\mathrm{K}^+]_{\mathrm{polym}}} \tag{2.1}$$

$$[\mathrm{TCNQ}^{\bullet-}\,\mathrm{K}^+]_{\mathrm{polym}} + \mathrm{e}^- + [\mathrm{K}^+]_{\mathrm{sol}} \rightleftarrows \underset{\text{(colorless)}}{[\mathrm{TCNQ}^{2-}\mathrm{K}_2^+]_{\mathrm{polym}}} \tag{2.2}$$

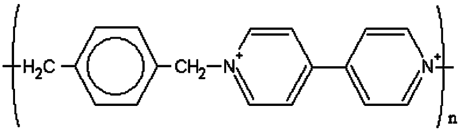
The subscripts “polym” and “sol” denote the polymer and solution phases, respectively.

These reaction formulae indicate that the electron transfer taking place at the metal|polymer interface is accompanied by ionic charge transfer at the polymer|solution interface, in order to maintain the electroneutrality within the polymer phase. Counterions usually enter the polymer phase, as shown above. However, less frequently the electroneutrality is established by the movement of co-ions present in the polymer phase, e.g., in so-called “self-doped” polymers. Oxidation reactions are often accompanied by deprotonation reactions, and H^+ ions leave the film, removing the excess positive charge from the surface layer. It should also be mentioned that simultaneous electron and ion transfer is also typical of electrochemical insertion reactions; however, this case is somewhat different since the ions do not have lattice places in the conducting polymers, and both cations and anions may be present in the polymer phase without any electrode reaction occurring. The establishment of equilibria and the different reaction and transport mechanisms involved will be discussed in Chaps. 5 and 6, respectively. For the sake of simplicity, only the electron transfer (redox transformation) will be indicated in some cases below.

In the case of the formation of TCNQ dimers, $\mathrm{TCNQ}_2^-\mathrm{K}^+$ and $(\mathrm{TCNQ})_2^{2-}\mathrm{K}_2^+$ (green) and the protonated species $\mathrm{TCNQH}^-\mathrm{K}^+$ and TCNQH_2 may also occur inside the polymer film.

2.1.1.2 Poly(Viologens) [22–26]

[Poly(*N*,*N*′-alkylated bipyridines]



Poly(xylylviologen)

Synthesis: α,α'-dibromoxylene + 4,4′-bipyridine [25].

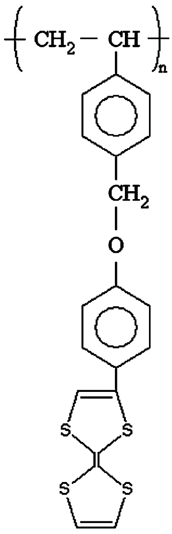
Redox reaction:

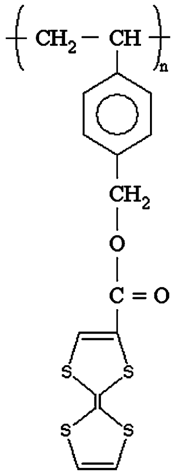
$$\begin{array}{lll} \mathrm{bipm}^{2+} + \mathrm{e}^- \rightleftarrows & \mathrm{bipm}^{\overset{+}{\bullet}}; \quad \mathrm{bipm}^{\overset{+}{\bullet}} + \mathrm{e}^- \rightleftarrows & \mathrm{bipm}\ \text{(bipyridine)} \\ \text{(colorless,} & \text{(intense color: green)} & \text{(weak color)} \\ \text{CT complex:} & & \\ \text{scarlet)} & & \end{array} \tag{2.3}$$

$$\begin{array}{lll} \mathrm{MV}^{2+} + \mathrm{e}^- \rightleftarrows & \mathrm{MV}^{+}; \quad \mathrm{MV}^{+} + \mathrm{e}^- \rightleftarrows & \mathrm{MV}\ \text{(methylviologen)} \\ \text{(colorless)} & \text{(intense color: blue,} & \text{(colorless)} \\ & \text{dimer: red)} & \end{array} \tag{2.4}$$

2.1.2 Redox Polymers with Pendant Redox Groups

2.1.2.1 Poly(Tetrathiafulvalene) (PTTF) [27–31]





Synthesis: poly(vinylbenzylchloride) + potassium salt of *p*-hydroxyphenyltetrathiafulvalene or other derivatives [30, 31].

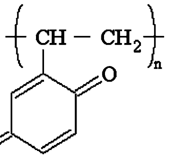
Redox reaction:

$$[\mathrm{TTF}]_{\mathrm{polym}} + [\mathrm{X}^-]_{\mathrm{sol}} \rightleftarrows [\mathrm{TTF}^{+\bullet}\mathrm{X}^-]_{\mathrm{polym}} + \mathrm{e}^- \tag{2.5}$$

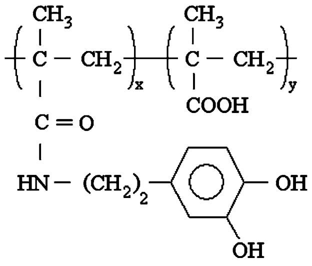
$$[\mathrm{TTF}^{+\bullet}\mathrm{X}^-]_{\mathrm{polym}} + [\mathrm{X}^-]_{\mathrm{sol}} \rightleftarrows [\mathrm{TTF}^{2+}\mathrm{X}_2^-]_{\mathrm{polym}} + \mathrm{e}^- \tag{2.6}$$

Also, formation of dimers: TTF_2^{+}, TTF_2^{2+}.

2.1.2.2 Quinone Polymers [32–38]



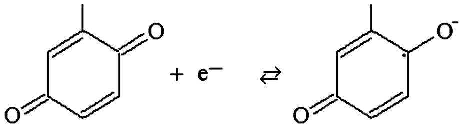
Poly(vinyl-*p*-benzoquinone)



Poly(acryloyldopamine)

Synthesis: radical polymerization of vinylbis(1-ethoxyethyl) hydroquinone [34] or by reaction of acryloyl chloride with dopamine [33].

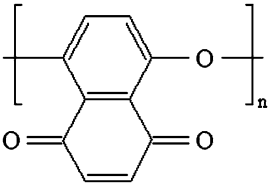
Redox reactions (in nonaqueous solutions) [32]:



(2.7)

(in aqueous solutions) [33]:

$$\text{hydroquinone form} \rightarrow \text{quinone form} + 2e^- + 2H^+ \tag{2.8}$$

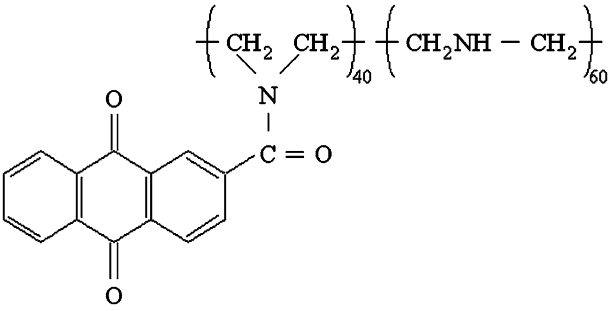


Poly(naphthoquinone) (PNQP)

Synthesis: electropolymerization of 5-hydroxy-1,4-naphthoquinone [38].

Redox reaction:

$$\mathrm{PNQP} + 2e^- + 2H^+ \rightleftharpoons \mathrm{PNQPH_2} \tag{2.9}$$



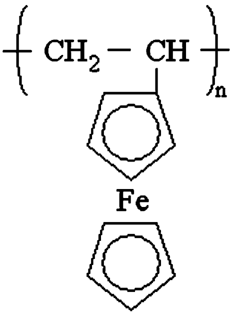
Poly(anthraquinone) (PQ)

Synthesis: poly(ethyleneimine) + 2-anthraquinone carbonyl chloride [36, 37].

Redox reaction:

$$\mathrm{PQ} + 2e^- + 2H^+ \rightleftarrows \mathrm{PQH_2} \tag{2.10}$$

2.1.2.3 Poly(Vinylferrocene) (PVF or PVFc) (Organometallic Redox Polymer) [39–75]



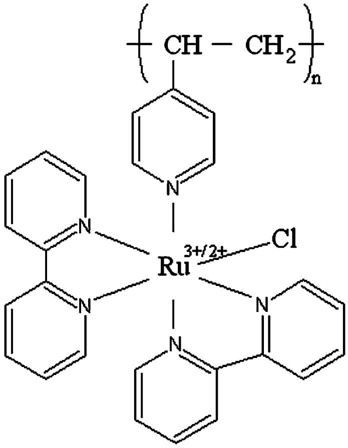
Synthesis: polymerization of vinylferrocene [73].

Redox reaction:

$$[\text{ferrocene}]_{\text{polym}} + [\text{X}^-]_{\text{sol}} \rightleftarrows [\text{ferrocenium}^+\text{X}^-]_{\text{polym}} + \text{e}^- \tag{2.11}$$

2.1.2.4 [Ru or Os (2,2′-Bipyridyl)$_2$(4-Vinylpyridine)$_n$Cl]Cl [76–83]

$[\text{Ru(bpy)}_2(\text{PVP})_n\text{Cl}]\text{Cl}, n = 5$



Also copolymers with styrene or methylmethacrylate; PVP was also replaced by poly-*N*-vinylimidazole [77–79, 83, 84].

Redox reaction [76–83]:

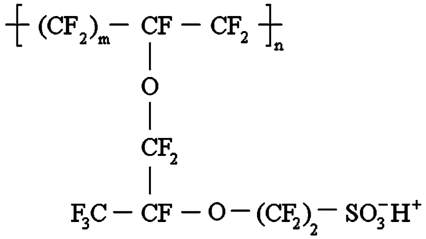
$$[\text{Ru}^{2+}\text{X}_2^-]_{\text{polym}} + [\text{X}^-]_{\text{sol}} \rightleftarrows [\text{Ru}^{3+}\text{X}_3^-]_{\text{polym}} + \text{e}^- \tag{2.12}$$

$$[\text{Os}^{2+}\text{X}_2^-]_{\text{polym}} + [\text{X}^-]_{\text{sol}} \rightleftarrows [\text{Os}^{3+}\text{X}_3^-]_{\text{polym}} + \text{e}^- \tag{2.13}$$

2.1.3 Ion-Exchange Polymers Containing Electrostatically Bound Redox Centers

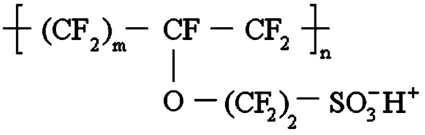
Usually the electrode surface is coated with the ion-exchange polymer, and then the redox-active ions enter the film as counterions. In the case of a cation-exchanger, cations (in anion-exchangers, negatively charged species) can be incorporated, which are held by electrostatic binding. The counterions are more or less mobile within the layer. A portion of the low molar mass ions (albeit usually slowly) leave the film and an equilibrium is established between the film and solution phases. Polymeric (polyelectrolyte) counterions are practically fixed in the surface layer.

2.1.3.1 Perfluorinated Sulfonic Acids (Nafion®) [85–105]



Synthesis: copolymerization of perfluorinated ethylene monomer with SO_2F containing perfluorinated ether monomer [88,91]; $m = 6 - 12$. Nafion® 120 (DuPont) means 1200 g polymer per mole of H^+, there are Nafion® 117, 115, 105, etc.

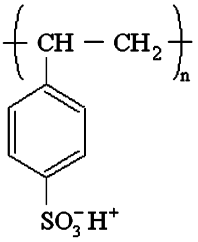
Dow ionomer membranes [89]:



Redox-active ions that have been extensively investigated by using Nafion-coated electrodes:

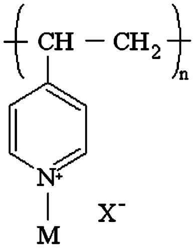
$Co(bpy)_3^{3+/2+/+}$ (bpy = 2,2′-bipyridine) [86, 87],
$Co(NH_3)_6^{3+/2+}$ [86] $Ru(NH_3)_6^{3+/2+}$ [86],
$Ru(bpy)_3^{3+/2+}$ [86, 87, 92, 94, 96, 98, 99, 102–105],
$Os(bpy)_3^{3+/2+}$ [85, 92, 100, 101],
Eu^{3+} [87],
ferrocenes$^{+/0}$ [98, 101], methylviologen ($MV^{2+/+/0}$) [90, 93, 98],
methylene blue [97], phenosafranin and thionine [95].

2.1.3.2 Poly(Styrene Sulfonate) (PSS) [106–113]



Redox ions investigated are as follows: Ru(bpy)$^{3+/2+}$, Os(bpy)$^{3+/2+}$ [106–114], Eu$^{3+/2+}$ [109].

2.1.3.3 Poly(4-Vinylpyridine) (PVP, QPVP) [115–127]



M = H, CH$_3$

In this cationic, anion-exchanger polymer, the following redox anions have typically been incorporated and investigated:

Fe(CN)$_3^{3-/4-}$ [116–118, 120–123, 125–127], IrCl$_6^{2-/3-}$ [116–119, 122, 126, 127], Mo(CN)$_8^{3-/4-}$ [126], W(CN)$_8^{3-/4-}$ [126], Ru(CN)$_6^{3-/4-}$, Co(CN)$_6^{3-/4-}$, Fe(edta)$^{-/2-}$, Ru(edta)$^{-/2-}$ [124].

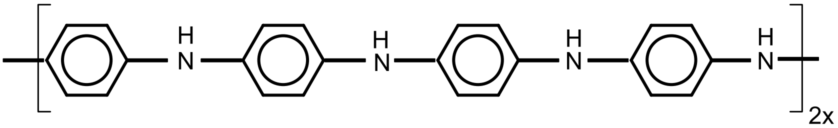
2.2 Electronically Conducting Polymers (Intrinsically Conducting Polymers—ICPs)

In the case of conducting polymers, the motion of delocalized electrons occurs through conjugated systems; however, the electron hopping mechanism is likely to be operative, especially between chains (interchain conduction) and defects. Electrochemical transformation usually leads to a reorganization of the bonds of the polymers prepared by oxidative or less frequently reductive polymerization of benzoid or nonbenzoid (mostly amines) and heterocyclic compounds.

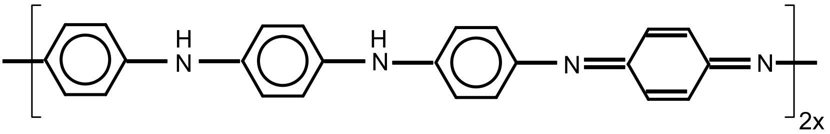
2.2.1 Polyaniline (PANI) and PANI Derivatives [128–348]

Idealized formulae of polyaniline at different oxidation and protonation states: L = leucoemeraldine (closed valence; shell reduced form; benzenoid structure); E = emeraldine (radical cation intermediate form; combination of quinoid and benzenoid structures); P = pernigraniline form (quinoid structure); LH_{8x}, EH^{1}_{8x}, EH^{2}_{8x} are the respective protonated forms:

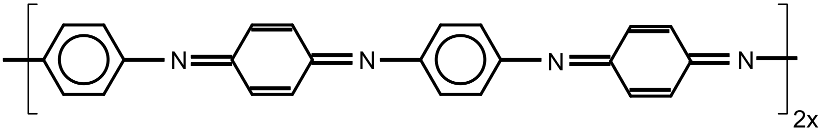
L



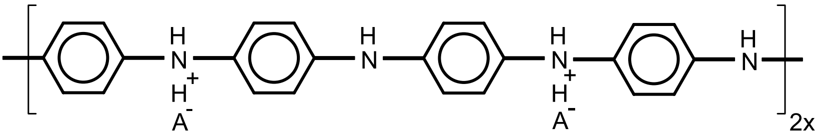
E



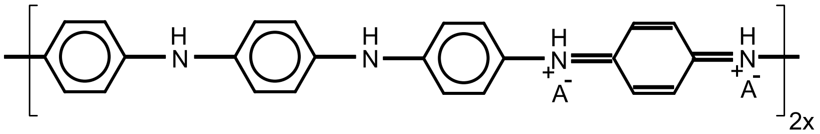
P



LH_{8x}



EH^{1}_{8x}



EH^{2}_{8x}

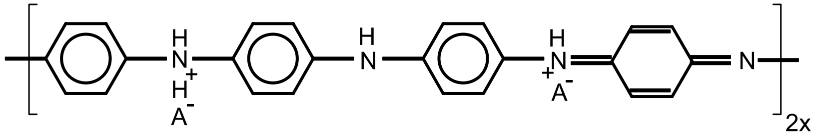
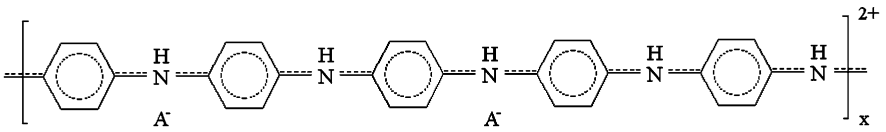
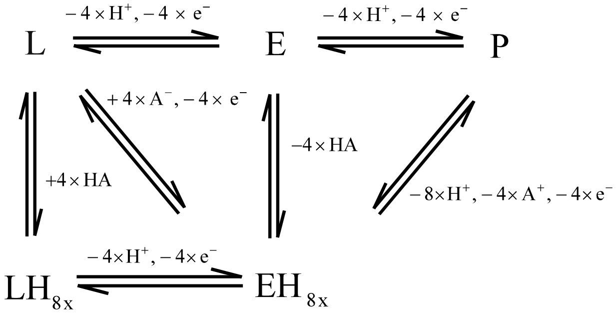


Illustration of delocalization (polaron lattice) of the emeraldine state:



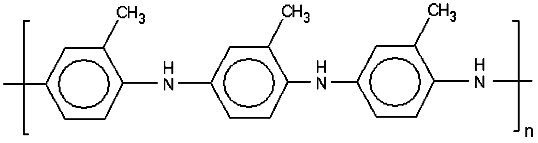
Synthesis: oxidative electropolymerization of aniline in acidic media [128, 133, 141, 157, 162, 168, 170, 184, 186, 189, 201, 215, 216, 222, 224, 250, 257, 261, 264, 278, 287, 296, 318, 320–324] or chemical oxidation by $Fe(ClO_4)_3$, $K_2S_2O_8$ [304, 305, 325, 326].

Redox reactions [142, 143, 147, 172, 220, 227, 243, 244, 274, 321, 327]:



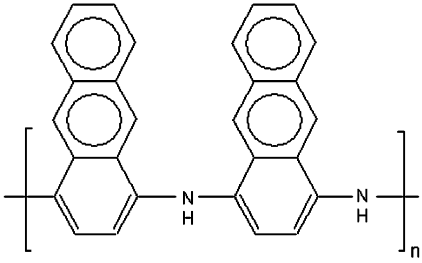
The color change during the redox transformations is as follows: yellow ⇄ green ⇄ blue (violet).

It should be mentioned that polymers that behave in a similar way to PANI can also be prepared from compounds other than aniline (e.g., from azobenzene [201]). Substituted anilines—especially the formation and redox behavior of poly(*o*-toluidine) (POT)—have been studied in detail [328–343].



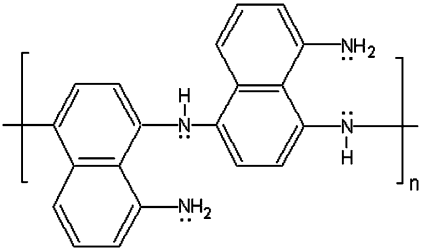
Poly(*o*-toluidine)

Polymers such as poly(*o*-ethoxyaniline) [344], poly(1-pyreneamine) [345], and poly(1-aminoanthracene) [346] have also been synthesized by electropolymerization from the respective monomers.

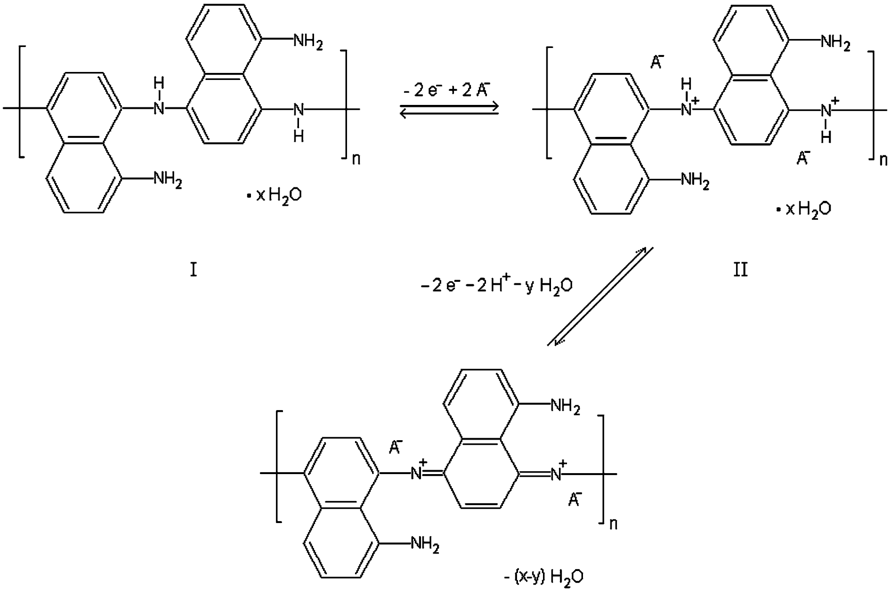


Poly(1-aminoanthracene)

Interestingly, the oxidative electropolymerization of 1,8-diaminonaphthelene leads to a polyaniline-like polymer; however, the second amine group of the monomer does not participate in the polymerization reaction [319]:



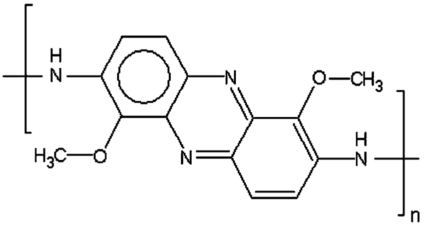
The redox transformations of poly(1,8-diaminonaphthalene) (PDAN) can be described by the following scheme:



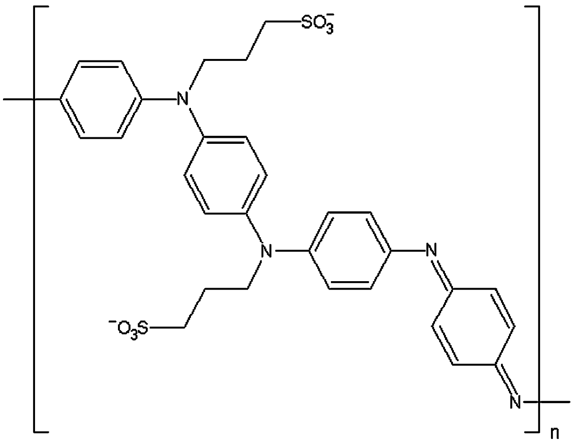
III

The oxidative polymerizations of other aryl amines yield polymers with ladder structures. We will discuss these polymers later (Sects. 2.2.3, 2.2.4, 2.2.13).

In the case of the electropolymerization of 2-methoxyaniline [347, 348] at high monomer concentrations, a PANI-like conducting polymer was obtained, while at low concentrations a polymer with phenazine rings was formed [347]:



Different "self-doped" polyanilines have been prepared using aniline derivatives containing carboxylate or sulfonate groups, or the acid functionalities were incorporated during a post-modification step using the appropriate chemical or electrochemical reactions [158, 197, 254, 303].

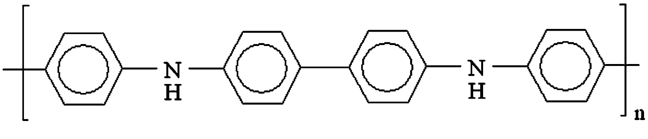


Poly(aniline-*co*-*N*-propanesulfonic acid-aniline)

Copolymers from aniline and another monomer (e.g., *o*-phenylenediamine [253]) or even from aniline and two other aniline derivatives [307] have also been electrosynthesized and characterized (see later).

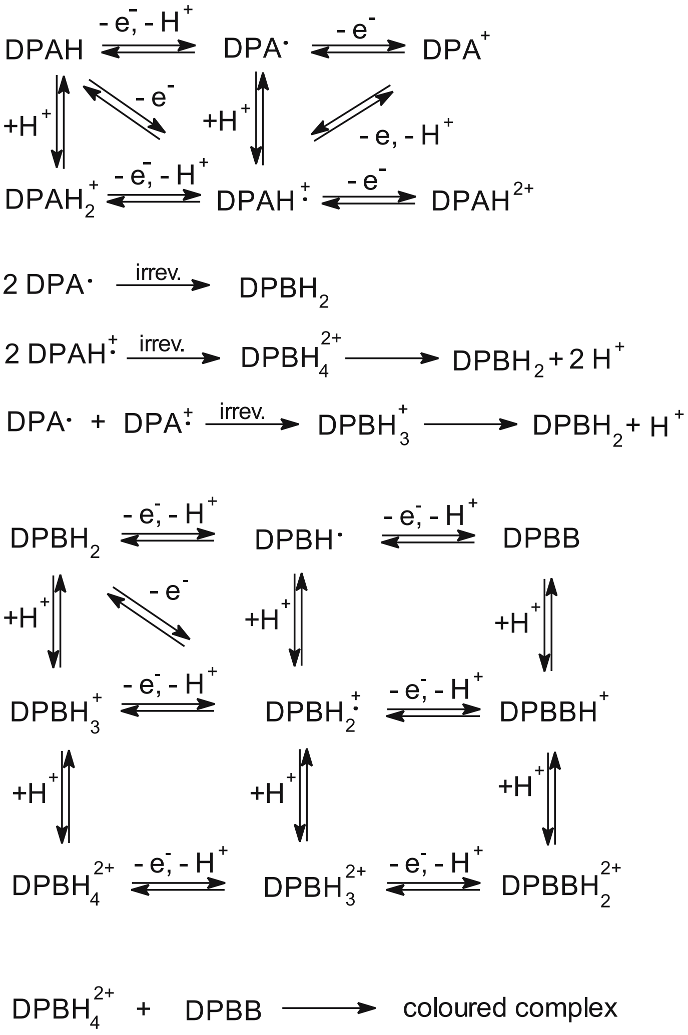
2.2.2 Poly(Diphenylamine) (PDPA) [349–362]

[Specifically, poly(diphenylbenzidine).]

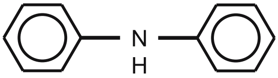


Synthesis: oxidative electropolymerization of diphenylamine in acid media [349–358].

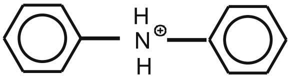
Redox reactions:



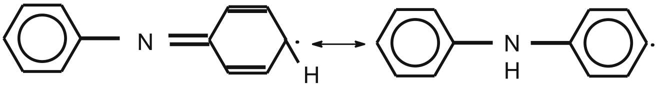
where



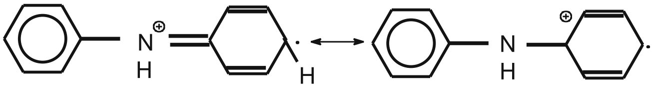
DPAH



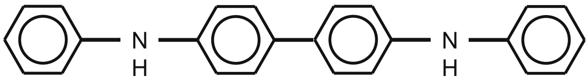
$DPAH_2^{+}$



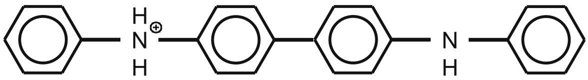
$DPA^{\cdot}$



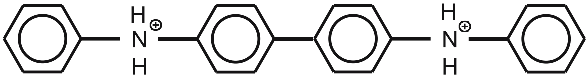
$DPAH^{+\cdot}$



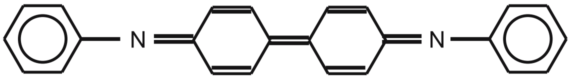
$DPBH_2$



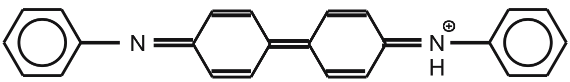
$DPBH_3^{+}$



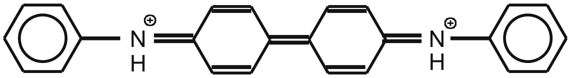
$DPBH_4^{2+}$



DPBB



$DPBBH^{+}$



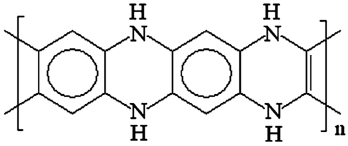
$DPBBH_2^{2+}$

Color change is colorless (reduced form) ⇄ bright blue (violet) (oxidized form) at pH 0.

A polymer with a similar structure and properties can also be obtained by the oxidative electropolymerization of 4-aminobiphenyl [356] or benzidine [353].

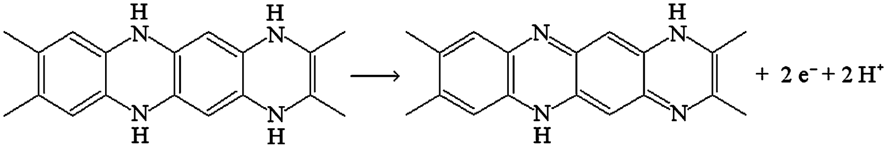
2.2.3 Poly(o-Phenylenediamine) (PPD) [363–390]

(In fact, PPD is a ladder polymer that contains pyrazine and phenazine rings.)

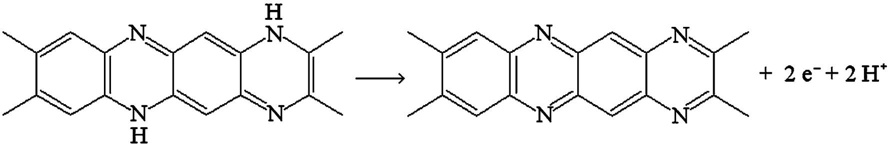


Preparation: oxidative electropolymerization of *o*-phenylenediamine [363–385], less frequently by chemical oxidation. A similar polymer can be prepared by the electropolymerization of 2,3-diaminophenazine [383].

Redox reaction:



(2.14)



(2.15)

Color change: colorless (reduced form) $\rightleftarrows$ red (oxidized form).

2.2.4 Poly(2-Aminodiphenylamine) (P2ADPA) [391]

P2ADPA contains phenazine and open-ring (PANI-like) units.