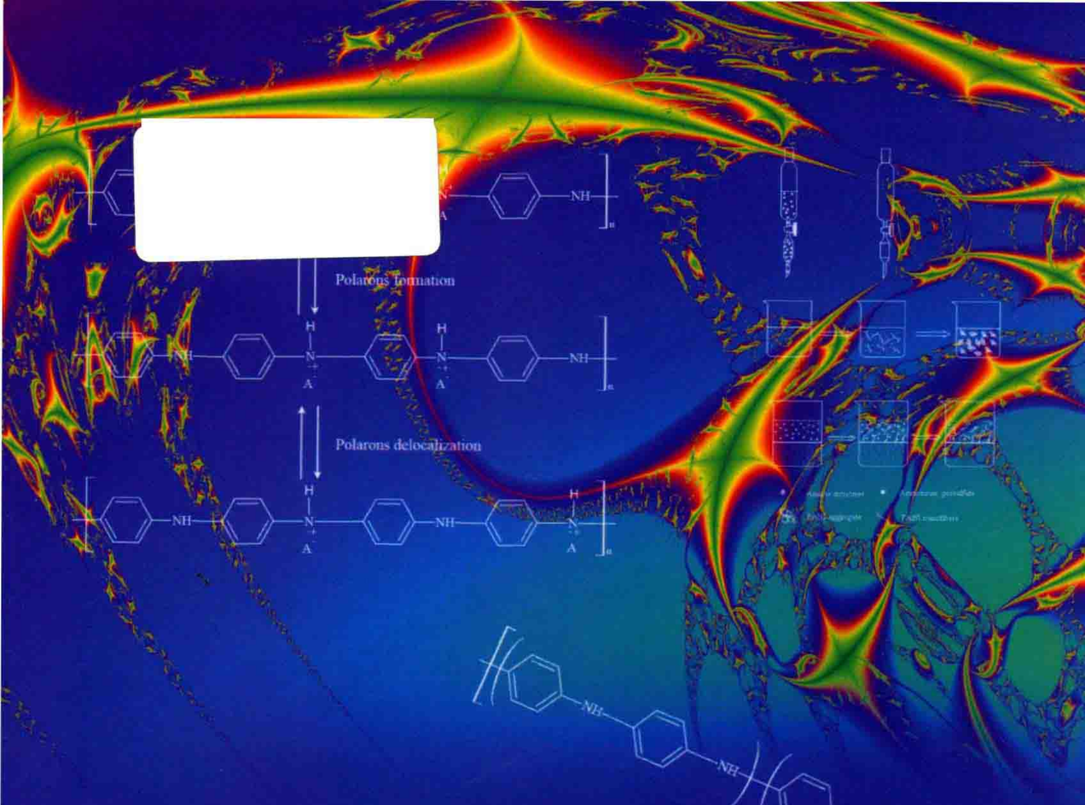

Cristina Della Pina
Ermelinda Falletta

Polyaniline

From Tradition to Innovation

Polymer Science and Technology

Novinka

POLYMER SCIENCE AND TECHNOLOGY

POLYANILINE

FROM TRADITION TO INNOVATION

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AND

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This Book is dedicated to our Mentor,
Professor Michele Rossi

Extraordinary Master of Science and Life
Forever grateful
Cristina & Ermelinda

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Cristina & Ermelinda

INTRODUCTION: POLYANILINE: THE IMPORTANCE OF STRUCTURE, CRISTALLINITY DEGREE, MOISTURE, MOLECULAR WEIGHT AND *DOPING* FOR TUNING CONDUCTIVITY

Among the intrinsically conducting polymers (ICPs), polyaniline (PANI) is one of the oldest and most investigated. Even though the date of the first synthesis is not sure, in 1834 Runge described a method to isolate from coal tar a substance that became blue colored when treated with chloride of lime and he named it kyanol or cyanol. [1] In 1856 by the oxidation of crude aniline in the presence of potassium dichromate the first synthetic dye, mauveine, was industrially obtained. [2-4] A black precipitate, known as "aniline black", was also observed in 1860. [5] It was a polymeric constituent of melanin. However, only the accurate investigations of Green and Woodhead allowed to better understand the properties of this surprising material. [6,7]

Over the years the interest in polyaniline has rejuvenated owing to its peculiar chemico-physical characteristics, such as unique doping/dedoping mechanism, environmental and thermal stability, and tuneable conductivity. This book will focus on polyaniline. After an introduction on its various structures available, with an emphasis on the importance of the different oxidation states, *doping* (protonation), degree of crystallinity, moisture and molecular weight for tuning conductivity, the main synthetic methods will be presented. They will range from the traditional protocols to the innovative eco-friendly routes which employ "green" oxidants and proper catalysts. Regarding the ultimate preparation methods, a particular focus will be dedicated to the starting reagents. It has been recently found how starting from the monomer (aniline) or the dimer (AD, *N*-(4-aminophenyl)aniline) deeply affects polymerization and properties of the final material, with important repercussions on the potential applications. The choice of the catalyst is also fundamental, thus another section will cover the state-of-the-art of the novel catalytic systems. The doping agents, degree of crystallinity and moisture, whose effects on PANI conductive capability are dramatic, deserve particular attention therefore recent findings on their influence over the final material performance will be mentioned as well. The possibility to combine the fascinating conducting properties of PANI with those of other materials has opened the way to the preparation of new amazing materials. In this context, organic–inorganic nanocomposites with organized structure have been extensively studied, because they combine the advantages of inorganic materials (mechanical strength, electrical and magnetic properties and thermal stability) with those of organic polymers (flexibility, dielectric behavior, ductility and processing). Accordingly, a chapter will describe the principal synthetic methods and properties of PANI-based composites. For completing the part dedicated to polyaniline blends, a special note will describe a brand new preparation protocol able to facilitate polymer processing into pure electrospun nanofibers. The main analytical techniques suitable for characterizing polyaniline and its composites will be collected in a further chapter. The spectrum of applications of PANI-based materials is wide, ranging from electrical and optical devices to sensors, as well as EMI shielding, anticorrosive and biomedical materials. A short description of two important accomplishments in this area will find place in a dedicated chapter, followed by the conclusion. Academics, researchers, scientists, engineers and students dealing with material science and nanotechnology are the target audience for this book.

THE IMPORTANCE OF STRUCTURE

Polyanilines refer to a class of polymers composed of repeated aniline units connected to each other to form a backbone, whose basic form has the general structure reported in Figure 1.

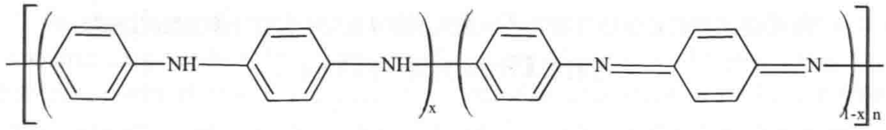

Figure 1. Polyaniline general structure.

The oxidation state (x) can vary from 1, giving the totally reduced form called *leucoemeraldine*, to 0.5 thus producing the half-oxidized form, *emeraldine*, as well as zero which leads to the completely oxidized form, *pernigraniline*. Besides these three main structures, further intermediate forms are available, such as *protoemeraldine*, characterized by an oxidation state intermediate between *leucoemeraldine* and *emeraldine*, and *nigraniline*, having an oxidation degree between *emeraldine* and *pernigraniline.* [8]

Each form can exist either as base or as protonated salts. However, only the protonated salt form of *emeraldine* (*emeraldine salt*, ES) is conductive. In fact, the complete protonation of the nitrogen atoms of imine groups leads to the formation of delocalized polysemi-quinone radical cations that increase the electronic conductivity of the polymer. Other chemico-physical properties of polyaniline are strictly correlated to its degree of oxidation, for example optical, electrical and thermal aspects.

More in detail, *leucoemeraldine* is an amorphous material with a white/pale brown colour, not stable under air and, if heated, it undergoes quick oxidization to *protoemeraldine.*

The colour of *protoemeraldine* ranges from violet in its base form to yellowish/pale green if protonated.

In its base form *emeraldine* is blue coloured and soluble in some organic solvents, as pyridine, *N*, *N*-dimethylformamide and *N*-methylpyrrolidinone. It becomes green after doping (protonation) with an acid. Undoped *nigraniline* is characterized by a dark blue coloration. This form is unstable at high temperature passing to the more stable form of *emeraldine.*

In its highest oxidation state, *pernigraniline*, polyaniline is not stable quickly decomposing to form lower oxidation state species.

However, among all the possible PANI structures, only the half-oxidized *emeraldine* exhibits conducting properties when it is protonated with inorganic or organic acids.

A GLANCE TO THE PARAMETERS INFLUENCING THE CONDUCTIVITY

The most intriguing property of polyaniline is being able to switch from an insulating state to a conducting one, thereby opening the way for many applications especially in electronics. In the last two decades scientists all over the world have suggested possible theoretical explanations for PANI conduction mechanism, proposing the heterogeneous disorder theory, [9] the phonon theory, [10] the band theory, hole and hopping theory, just for citing the principal ones. However, the ability of PANI to conduct electricity is the sum of many factors and, therefore, several parameters have been monitored, such as the oxidation degree of polymeric chains, the doping level, the crystallinity degree, the humidity level and the molecular weight. More emphasis on all these aspects will be given in Chapter 1. In principle, after protonation, the partially oxidized form of *emeraldine* undergoes an electron rearrangement thus producing stable radical cations, called polarons, that are the real active centres in the conducting process. Figure 2 displays the rearrangement of electrons in the backbone of *emeraldine* salt.

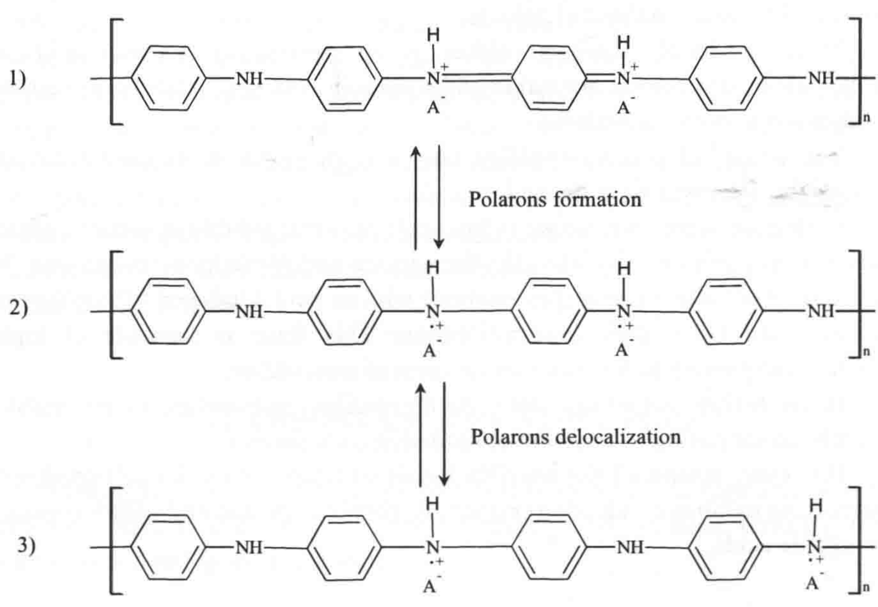

Figure 2. Electrons rearrangement in the backbone of *emeraldine* salt.

In step 1 an electron is transferred from each imine nitrogen into the aromatic ring leading to a benzenoid system. On each nitrogen atom this process leaves a single unpaired electron, that represents a radical cation, called polaron, that is unstable, and for this reason evolves towards the formation of two polarons (Figure 2, steps 2 and 3). The polaron lattice is responsible for the conductivity of polyaniline. [11]

Differently from other conducting polymers, characterized by a n-type and a p-type doping, the main doping process of polyaniline consists of a polymer protonation with Brønsted acids (protonic acid doping). In this context, the correlation between pH of the solution and increase of electrical conductivity in *emeraldine* salt, as well as the influence of the type of dopant on conductivity values were pointed out. [12] The crystallinity degree dramatically affects the electrical properties of polyaniline as conductivity increases with crystallinity, owing to a more organized structure of the polymeric chains. [13]

The correlation between conducting properties and humidity level was investigated by many researchers that suggested different models to explain the positive effect of water molecules on PANI conductivity. [14, 15]

Regarding the molecular weight, it has been found that too long chains can entail a number of structural imperfections, such as distortions and branching, thus depressing the polymeric conductivity. [16]

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