

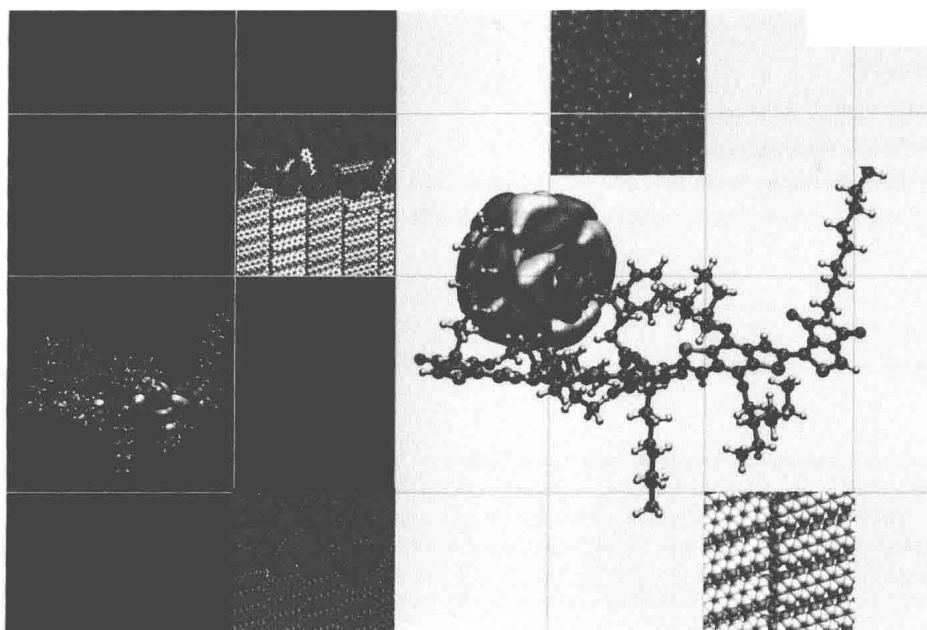
MATERIALS AND ENERGY – Vol. 7

# THE WSPC REFERENCE ON ORGANIC ELECTRONICS: ORGANIC SEMICONDUCTORS

**② Fundamental Aspects of Materials and Applications**

Editors

Seth R. Marder • Jean-Luc Bredas



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## ② Fundamental Aspects of Materials and Applications

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# CHAPTER 1

## CONDUCTING POLYMERS: REDOX STATES IN CONJUGATED SYSTEMS

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In this chapter, a brief history of conjugated polymers is presented followed by fundamental aspects of doping and redox states. The doping of polymers via either chemical dopants or electrochemical methods is outlined mechanistically for degenerate ground state, and non-degenerate ground state, conjugated systems with polaron and bipolaron formation, and the corresponding change in electrical conductivity discussed. Electrochromic polymers are presented to illustrate redox switching as the electrochemical process can be visualized through a visible color change. Additionally, the use of steric interaction to tune both the redox properties and color of a conjugated backbone is taught.

### 1. Setting the Stage

As we consider the many unique properties of  $\pi$ -conjugated organic molecules, oligomers, and polymers, it is evident from the previous chapters in this text that they behave as semiconductors in their neutral form, which provides many opportunities as electroactive materials. In this text we have been exposed to the properties of charge transport, light emission, and light absorption, which can all be finely tuned via molecular and macromolecular structure, allowing many potential applications to emerge. These applications include, but are not limited to, light emitting diodes, field effect transistors, organic solar cells, and photodetectors. In this chapter, we detail the importance of the creation of charged states on conjugated polymer chains and how these charged states provide a different set of properties not accessed in the neutral systems alone.

Reflecting historically on the development of  $\pi$ -conjugated active materials one can start with research from the 1970s in the preparation of free-standing films<sup>1</sup> of polyacetylene  $(\text{CH})_X$  and its oxidative doping to attain high levels of electrical conductivity.<sup>2,3</sup> This research carried out in the research groups of Hideki Shirakawa,

Alan MacDiarmid, and Alan Heeger provided the crucial discoveries that stimulated and helped to create the field of conjugated polymers and ultimately led to the awarding of the Nobel Prize in Chemistry in 2000.<sup>4</sup> This story has been related in many reviews and publications<sup>4-6</sup> and will not be repeated here. Rather, we will use that work to guide us as we discuss the fundamental aspects of the charged states of conjugated polymers. It should be noted that while this material can be synthesized in either a *cis* or *trans* configuration,<sup>3</sup> with correspondingly different properties, we will be focusing on the *trans* form in this text.

Silver colored, free-standing films of  $(\text{CH})_X$  can be prepared via Ziegler-Natta (ZN) polymerization of acetylene on a surface coated with ZN-catalyst/initiator system.<sup>1</sup> While these films are easily handled and can be cut to any dimension, it is important to note that they are air unstable as they oxidize in an ambient atmosphere. This property of low oxidation potentials is actually a benefit as we consider the next step in generating electrical conductivity in a conjugated polymer. The as-made  $(\text{CH})_X$  films are semiconducting in nature with the all *trans* isomer having electrical conductivities on the order of  $10^{-5}$  S/cm.<sup>2</sup> Placing these films in a vacuum reactor with electrical leads attached and subsequently exposing them to gas-phase oxidants (such as  $\text{I}_2$  or  $\text{AsF}_5$ ) leads to an immediate and large enhancement of the electrical conductivity with over an eight order of magnitude change measured in the first experiment to conductivities greater than 20,000 S/cm. For example, Park and co-workers carried out the ferric perchlorate oxidation of  $(\text{CH})_X$  to provide materials with conductivities ranging between 20,000–41,000 S/cm.<sup>7</sup> These oxidation experiments can be also be carried in both solution and electrochemical methods as exemplified by perchlorate doping.<sup>8,9</sup>

These oxidation reactions are often termed “doping” by analogy to the doping of inorganic semiconductors with trace additives as similar changes in conductivity are observed. This is evident in Fig. 1 for results provided on poly  $[(\text{CH})_X-\text{ClO}_4]$  prepared by electrochemical oxidation in a perchlorate electrolyte.<sup>8</sup> During this oxidation, as charges are introduced onto the polymer backbone a charge balancing counter ion, the so-called dopant ion, is introduced into the material and its content can be measured allowing establishment of a dopant level. In these experiments the doping level ( $Y$ ) is controlled over five orders of magnitude from one charge per million carbon atoms in the  $(\text{CH})_X$  film, to one charge per ten carbon atoms. At low doping levels, it can be seen that the conductivity stays between  $10^{-6}$ – $10^{-5}$  S/cm, up to approximately one charge per 10,000 carbon atoms. Near a dopant level of one charge per thousand carbon atoms, an especially rapid increase in conductivity is found to occur to values near 100 S/cm. This rate of increase then begins to decline upon further doping.

So, what is happening during this oxidative doping process? Figure 2(a) shows a two-step oxidation process of  $(\text{CH})_X$ . Starting with the neutral polymer, initial removal of electrons from the conjugated backbone leads to cation-radicals randomly distributed along the polymer chain, which are counter balanced by the dopant anions  $X$ . With these initial oxidations, these cation-radicals remain





will coulombically repel one another and leads to an upper dopant level of about one charge per 7–10 carbon atoms (in the case of polyacetylene). At first glance, one might be surprised that such a large conductivity increase is observed when there is only one charge per thousand carbon atoms in the material. Consider though that these thousand carbon atoms can fit in a box 10 carbon atoms long per side. On average then, each charge is only on the order of five carbons away from the “box” that the next charge can be found in. The very rapid rise in conductivity can then be attributed to an immediate and rapid increase in the mobility of the charges as conductivity, in a simple sense, is a product of the number of charges, their mobility, and the magnitude of the charge on the carrier. The conductivity in these oxidatively doped  $(\text{CH})_x$  materials is  $p$ -type as the positive carriers on the polymer chains are mobile, while the dopant anions are immobile in the solid film. Many  $p$ -type dopant systems and methods have been developed over the years.<sup>10</sup> Of particular note is the work of Marder *et al.* on molybdenum-based  $p$ -dopants. These dopants were thoroughly investigated using both experimental and computational techniques and found to be versatile and stable in devices.<sup>11–13</sup>

Analogous to  $p$ -doping, chemical or electrochemical reduction of  $(\text{CH})_x$  can lead to the formation of radical anions and delocalized anionic charge carriers to form  $n$ -type doped materials. This is illustrated in Fig. 2(b) where the mobile charge carriers are the anions delocalized along the polymer backbone. Early experiments used especially reactive reducing agents, such as elemental sodium and potassium in naphthalene, to provide the  $n$ -doped materials with the alkali metal cations as the charge balancing species.<sup>14</sup> These dopant systems are difficult to handle, as they require full exclusion of ambient oxygen and moisture. This has motivated research in the field to develop new stable dopant systems. Marder and co-workers have led the way in this research area by their studies on  $n$ -dopants that are stable to oxygen in the solid state.<sup>15</sup> The focus of this work has been in using ruthenium and rhodium-based dimers as reductants that form stable cations in films or solutions.

Examining the structure of neutral trans  $(\text{CH})_x$ , it can be observed to have what is termed a degenerate ground state.<sup>16</sup> What this means, in essence, is that the resonance form shown for the double bonds on the main chain in Fig. 2(a) have the same energy as the resonance form that can be drawn by moving each electron pair over one bond. In comparison to benzene, one would think that the polymer might have a bond order of 1.5 and that the electrons along the  $(\text{CH})_x$  chain would be fully delocalized in the neutral polymer with all bonds being the same length. This is not the case as there is a stabilization of the structure to form long and short bonds (short bonds not as short as double bonds and long bonds, not quite as long as single bonds) due to a Peierls transition, which is similar in concept to the Jahn–Teller effect.<sup>17</sup> The length of these long bonds and short bonds have been measured by electron diffraction and shown to be 1.38 and 1.43 Å in length for the double and single bonds, respectively.<sup>18</sup> The result in this degenerate ground state system is that the charge carriers formed on the fully oxidized or reduced material move independently along the polymer chain, coulombically repelling one another