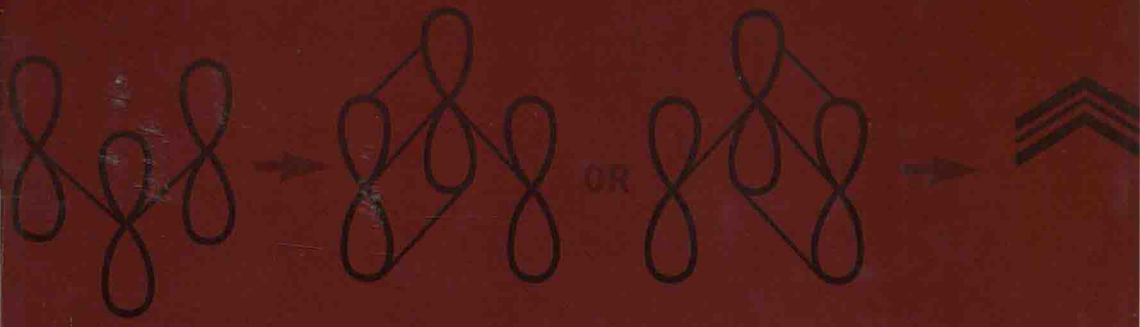
DOPING IN CONJUGATED POLYMERS

Pradip Kar



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The book is dedicated to my family

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Preface

The versatility of polymer materials has expanded as electroactive behavior has been included in the characteristics of some of the polymers. The most exciting development in this area is related to the discovery of intrinsically conductive polymers or conjugated polymers. Some examples are polyacetylene, polyaniline, polypyrrole, polythiophene, etc., as well as their various derivatives. The conjugated polymers which are a field of interest for researchers are also well known as "synmet" or "synthetic metal" due to the incorporation of some metallic characteristics, i.e., conductivity. Interest in this field is increasing day by day after the awarding of Nobel Prize for the discovery and development of electrically conducting conjugated polymers in the year 2000 by three scientists: Prof. Alan J. Heeger, Prof. Alan G. MacDiarmid and Prof. Hideki Shirakawa. Generally, the conductivity of these undoped conjugated polymers is 10^{-7}-10^{-11} S cm^{-1}. But for the application of conjugated polymers instead of inorganic or traditional semiconductors some higher conductivity is required. The conductivity of conjugated polymers, which are either weak semiconductors or insulators, increases by several folds due to "doping." These conjugated polymers convert to a conductor or semiconductor from the insulator or low semiconductor by doping. Although the conductivity of doped conjugated polymers is higher than that of saturated insulating polymers, it is much less than that of conducting metals, e.g., Cu, Ag, Au, etc., and most of the doped conjugated polymers show conductivity in the semiconducting region. However, it is universally agreed that the doping process is an effective method to produce conducting polymers. As doping makes a semiconducting polymer from an insulting or low conducting one, it is of very much importance for the real applications of the conjugated polymers as semiconducting material.

The performance of doped conjugated polymers is greatly influenced by the nature of dopants and their level of distribution within the polymer. Therefore, the electrochemical, mechanical, and optical properties of the doped conjugated polymers can be tailored

by controlling the size and mobility of the dopants counter ions. The essential idea about the unusual nature of the species bearing charges, i.e., excited doped states of the conjugated systems, has been intensively discussed in the last twenty years. In this context the understanding of the nature of interaction by dopant with the π-conjugated systems is of foremost importance from the real application point of view. This rapid growth of interest in conjugated polymer-dopant interaction has been stimulated due to its fundamental importance to a cross-disciplinary section of investigators, chemists, electrochemists, biochemists, experimental and theoretical physicists, and electronic and electrical engineers. Finally, I wish to extend my sincere thanks and gratitude to all who helped me complete this project.

Pradip Kar

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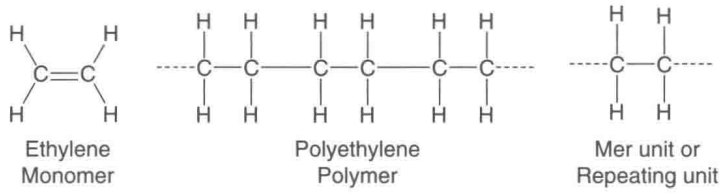
Introduction to Doping in Conjugated Polymer

1.1 Introduction

Recently, polymers have become the most widely used, versatile material on earth. This is due to some of the advantages they have over other materials such as flexibility, tailorability, processability, environmental stability, low cost, light weight, etc. [1]. Polymers are macromolecules which are formed by the repetitive union (mer unit or repeating unit) of a large number of reactive small molecules in a regular sequence. The simplest example is polyethylene, where ethylene moiety is the "mer or repeating unit" (Scheme 1.1). A major percentage of polymers are generally made up of carbon and hydrogen atoms with a minor percentage of some heteroatoms such as nitrogen, oxygen, sulfur, phosphorous, halogens, etc. In general, polymer is more than a million times bigger with respect to its size and molecular weight than that of small molecular compounds. The properties of polymers depend on their chemical composition, molecular structure, molecular weight, molecular weight distribution, molecular forces and



Scheme 1.1 Monomer and repeating unit for polyethylene.

morphology. Even in the fifth decade of the last century polymers were well known as electrically insulating materials. In modern civilization, polymers have been used as insulating cover on electrical wire, insulating gloves, insulating switches, insulating coatings on electronic circuit boards, low dielectric coatings, etc. [1]. The so called insulating polymers generally have a surface resistivity higher than 10^{12} ohm-cm. The polymers are insulating in nature due to the saturated covalent long-chain carbon framework structure or saturated covalent long-chain framework of carbon and some heteroatoms such as nitrogen, oxygen, sulfur, phosphorous, halogens, etc. In these polymers, the nonavailability of free electrons is responsible for their insulating behavior [2].

The versatility of polymer materials has expanded as electrochemical behavior has been included in the characteristics of some of the polymers. The electrochemical behavior means the mode of charge propagation, which is linked to the chemical structure of the polymer. In short, the chemical change within the polymer can help charge propagation, or the polymer can carry the charge through its chemical structure. The composites of conducting particles (carbon, graphite, metal, metal salt, etc.) with insulating polymers also show electrochemical behavior [3], e.g., composites of polyethylene oxide [4], polyethylene adipate [5] or polyethylene succinate [6] with Li salts. However, these materials are electrochemically active due to the electron transport within the conducting filler. In a true sense, the polymers themselves are not electrochemically active in these conducting composites. Based on the mode of