

# Conducting Polymers and Their Characterization

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**Abstract** - Polymer is a large molecule, formed by repeated linking of small molecules called 'monomers'. The technological development of the society largely depends on the materials. The search of new material led to the preparation of conducting polymers. Researches in the field of conducting polymers have attracted considerable attention for more than 40 years. Doped conducting polymers – especially polypyrrole and polyaniline have shown substantial attention because of their better environmental stability, good electrical conductivity and economical importance.

Keywords: Conductive Polymers, Dope, Polymerization

## 1. INTRODUCTION

Most of the polymers are used for electrical insulation, as they are bad conductor of electricity. Since these polymers do not possess large number of free electrons, they do not conduct electricity. Conductivity in polymers is observed because of different reasons. Accordingly they can be categorized into different types. Electrical conductivities are shown by few polymers because of its fundamental characteristics. Such polymers are known as intrinsically conducting polymers. These polymers have extensive conjugation in the backbone which is responsible for conductance. These polymers can be easily oxidized or reduced as they have low ionization potentials and high electron affinities. Their conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. This is called doping. Before the discovery of polyacetylene in 1977, conventionally polymers have been associated with no conducting properties and are used as insulators of metallic conductors, which resulted, introduced developments in the field of conducting polymers [1]. Polyacetylene is type of conjugated polymer, could become highly electrically conductive after undergoing a structural modification process called doping [2, 3]. The polymer is called a 'conjugated

polymer' because of the alternating single and double bonds in the polymer chain. Due to the special conjugation in their chains, it enables the electrons to de-localize throughout the whole system and thus many atoms may share them. The de-localized electrons may move around the whole system and become the charge carriers to make them conductive. This polymer can be transformed into a conducting form when electrons are removed from the backbone resulting in cations or added to the backbone resulting in anions. Anions and cations act as charge carriers, jumping from one molecule to the next in the effect of an electrical field, hence increasing conductivity. Out of the conducting polymers, specially conjugated conducting polymers polypyrrole and polyaniline have shown more attention worldwide because of their better thermal, chemical and environmental stability and excellent electrical conductivities. Doped polypyrrole and polyaniline have shown electrical conductivity in between  $10^{-5}$  S/cm &  $10^2$  S/cm, whereas common insulator show conductivities below  $10^{-12}$  S/cm. Under the consideration of protonation process in polypyrrole and polyaniline [4-5], solubility in common organic solvents and compatibility with various matrix polymers on the nanometer scale can be improved. In most of the cases poly acetylene is the simplest conducting polymer, in which the electrical transport properties are gained by keeping the conjugated polymer structure direction on the back bone of polymer [6]. Polyaniline, Polyparaphenylene, Poly3hexythiophone, poly (3-hlinr dioxinophne), Poly acetylene, polypyrrole and polythiophene are some common polymers. In future, conducting polymers or organic metals may replace inorganic metal in several critical areas. Certain aspects of the inorganic metals, such as not being environmentally friendly and having a high toxicity, are the reason why these organic metals have potential benefits as substitutes. The potential applications of these organic metals include corrosion protection, radars, batteries, sensors, as well as electro chromic cells.

## 2. OBJECTIVE

*General objective:* To study conducting polymers and their characterization.

*Specific object:* The main focus on study the specific objectives like; historical background, semiconducting

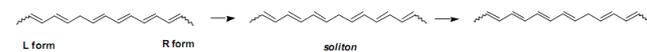
behavior, structural features, understanding the application of conducting polymers and the characterization of conducting polymer.

### 3. HISTORICAL BACKGROUND

Conducting polymer research dates back to the 1960s, when Pohl, Katon, and their coworkers, first synthesized and characterized semiconducting polymers [7]. The discovery of the high conductivity of polysulfurnitride (SN), a polymeric material containing interesting electrical properties, was a step forward for research in conducting polymers. The beginning of conducting polymer research started around 40 years ago, when films of polyacetylene were found to exhibit profound increases in electrical conductivity when exposed to halogen vapor [8]. J. Heeger, H. Shirakawa and G. MacDiarmid discovered conjugated conducting polyacetylene when monomer of acetylene was doped with bromine and iodine vapor; the resulting electrical conductivity was 10 times higher than the undoped monomers'. They were awarded Nobel Prize in Chemistry, 2000, for their discovery.

which  $\pi$  bonding electrons are spread over a number of atoms rather than localized between 2 atoms. This condition permits electrons to travel more easily making the electrically conducting polymers. When the  $I_2$  oxidative dopants is added, it takes away an electron from the  $\pi$  backbone of the polyacetylene chain and creates a positive charge (hole) on one of the carbon, now positively charged, is termed as a radical cation or **polaron**. The lone electrons of  $\pi$  bond, from where an electron was taken, can travel easily. As a moment the double bond moves along the molecule. A bipolaron is formed on further oxidation. If the polyacetylene chain is heavily oxidized, polarons condense pair-wise into so-called **solitons**. Mobile charged solitons which enable "spineless" conductivity are unique to polyacetylene.

Here, conducting polymers Poly (acetylene) & Polyaniline are taken as example to show principle of conduction mechanism.

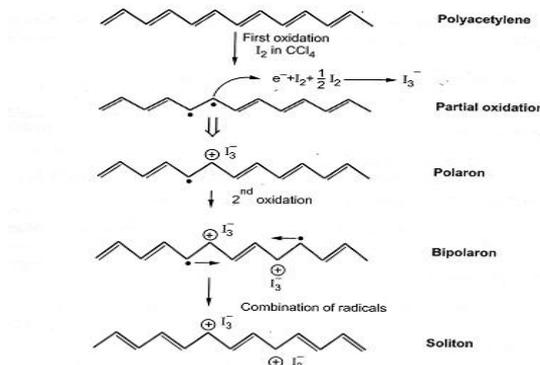


By showing the uniqueness property of unevenness of the poly (acetylene) in ground state, two corresponding polyene chains R and L are interconverted through the involvement of a mobile charge carrier, a soliton. The solitons are mobile charged or neutral defect, or a "kink" in the poly(acetylene) chain that spread down the chain and thus decrease the barrier for inter conversion.[9,10,11]

	S/cm		
Doped trans (CH), $10^5$ S/cm Doped polyaniline $10^3$ S/cm	$10^6$	Ag, Cu	Metals
	$10^2$	Fe	
	$10^4$	Mg	
	$10^2$	In, Sn	
	$10^1$	Ge	
Undoped trans (CH), $10^{-6}$ S/cm	$10^0$		Semimetals
	$10^{-2}$		
	$10^{-4}$		
	$10^{-6}$		
	$10^{-8}$		
Undoped polyaniline $10^{-10}$ S/cm	$10^{-8}$	Si	Insulators
	$10^{-10}$	AgBr	
	$10^{-12}$	Glass	
	$10^{-14}$	Diamond	
	$10^{-16}$	Nylon	
	$10^{-18}$	Quartz	
	$10^{-20}$		

Figure 1. Conductivity comparison between conductive polymers and other materials

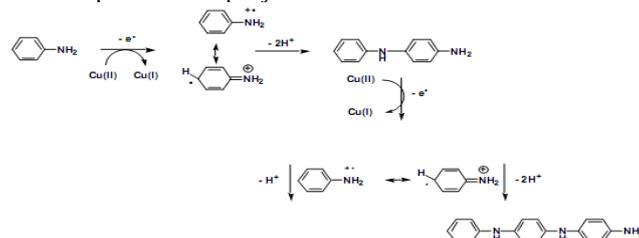
After their discovery, research papers dealing with polyconjugated systems were very extensive and systematic. The trend was to understand the chemical and physical aspects, either in neutral (undoped) state or charged (doped) states. According to Scifinder, almost 40,000 scientific papers were published in this field of research since 1977 [8]. This previously underestimated family of macromolecular compounds turned out to be extremely interesting, from both the basic research and application points of view.



Poly (aniline) s Polyaniline can be easily synthesized with a good yield by polymerizing aniline in protonic acid aqueous solution in the presence of an oxidant. It can be regarded as a conducting polymer under certain stimulating conditions like UV light, heat or addition of suitable dopant to the polymer.

### 4. CONDUCTION MECHANISM AND STRUCTURES OF CONDUCTING POLYMERS:

Conducting polymers are responsible for flow of electricity because of their conjugation in  $\pi$  bond system. Due to delocalization of electrons in molecule the conjugated double bands allow to flow of more number of electron. Delocalization is the condition in



Polyaniline exists in the three forms of oxidation states:

i) Pernigraniline (fully oxidized or only quinoid imine structure),

ii) Emeraldine (neutral or partially reduced and partially oxidized) and

iii) Leucoemeraldine (fully reduced or only benzenoid amine structure)

The emeraldine based (EB) form of polyaniline was used because only doped EB polyaniline is conductive among the three oxidation states. The emeraldine based form of polyaniline is the most stable of the three states because leuco-emeraldine is easily oxidized when exposed to air and pernigraniline is easily degraded.

The extended  $\pi$  bond system of conjugated polyaniline is highly susceptible to chemical & electrochemical oxidation or reduction. These alter the electrical and optical properties of the polyaniline, and by controlling this oxidation and reduction, it is possible to precisely control these properties.

## 5. CHARACTERIZATION TECHNIQUES

By analytical point of view, conducting polymers can be characterized in various ways. For e.g.:

i) Cyclic voltammetry-Particularly useful for redox processes in conducting polymers.

ii) Optical characterization of conducting polymers-for electro chromic window & non-linear optical materials.

iii) NMR - Useful for chain orientation, molecular motion and structure confirmation.

iv) Gel permeation chromatography-for molecular weight.

v) Raman analysis- for vibrational assignments.

vi) Differential scanning calorimetric & thermogravimetric analysis - for evidence of glass and melting transitions & decomposition temperatures.

vii) Dependence of conductivity on temperature, electric field and magnetic susceptibility -in order to understand the conductivity mechanism.

viii) Electroluminescence -to screen for potential use in light emitting diodes (LEDs).

ix) X-ray analysis including Rutherford back scattering to understand the crystal structure & to obtain elemental depth profiles, in order to gain insight into the conductivity mechanism.

## 6. PRESENT AND FUTURE POTENTIAL APPLICATIONS

Conducting polymers (CPs) have been used for many applications due to their chemical, mechanical, optical and electrical properties. Their semiconductor properties allow conjugated polymers to be used particularly in large area, such as electrochromic devices (EDCs), rechargeable batteries, light emitting diodes (LED's), field effect transistors (FET's), photovoltaic cells and chemical sensors [12]. Since conducting polymers change properties by incorporation of ions

and solvents (the property change easiest to measure is conductivity), it is possible to develop and market ion-specific sensors based upon conducting polymers. Conducting polymers could permit the incorporation of sensors into clothing. There are some challenges involved, such as background noise due to water absorption, lifetime, selectivity, and sensitivity. G. MacDiarmid first suggested the corrosion-inhibiting property of conducting polymers in 1985. Initial studies on the protection of metal surfaces against corrosion by conducting polymers were reported in the literature that same year. A major type of corrosion occurs by oxidation of a metallic surface by a water medium to produce oxides and hydroxides. As these are formed, soluble species are produced, the surface pits increase their surface area, and the rate of decomposition accelerates. One way to provide corrosion protection is to coat the metal with a barrier to prevent the reactive species from reaching the surface. Galvanization with zinc (or other metals with low oxidation potential) prevents corrosion via the creation of an interfacial potential at the metal-zinc interface. The zinc will corrode preferentially. While the reactive species may encounter the metal, the increased oxidation causes the metal to be insensitive. Corrosion is therefore inhibited. There was a great deal of initial excitement about conducting polymers as active materials in batteries. Owing to their low density, it was thought that a battery with power densities much higher than those of the ordinary lead/acid battery could be readily obtained. Since the charge on a polymer backbone is distributed over three or four repeat units, the charge capacity per unit of mass for conducting polymers is marginally better than that of metals. Conducting polymer batteries were investigated by BASF/VARTA and Allied Signal. Bridgestone has marketed a button-sized battery using polyaniline and lithium. Conducting polymer still has a potential use in lithium-based high-power density batteries, which use the high potential difference between lithium and the polymer to achieve high power densities, although stability and shelf life are still issues. As more and more individuals utilize cellular phones, laptop computers, and cordless drills, the importance of batteries that will handle many deep cycles (at least 60% depth of discharge) becomes increasingly apparent. Conducting polymer-based batteries show promise, but much work needs to be done. A significant event occurred when Friend et al [13] published an electroluminescence study on the neutral (non-conducting) form of paraphenylenevinylene. This work has opened up a new avenue of research and, more importantly, a potential market for the material.

Several articles on conducting polymer LEDs and the effect of various additives, electrode modifications, tuning emission, the effect of impurities, and discussions of hole tunneling, photo excitation, and unusual symmetric bias, have been published. The efficiency of LEDs is constantly being improved along with novel developments such as flexible LEDs, polarized light-emitting LEDs and light emitting electrochemical cells.

The emission of red, green, blue and white light have all been demonstrated, and so has brightness of the order of 400 cdm<sup>-1</sup>, which is similar in brightness to fluorescent lights or computer displays. Conducting polymers enable a wide variety of structures to be synthesized and therefore many different wavelengths of light are possible. Although conducting polymers will not replace fluorescent light bulbs (which have efficiencies of around 70%), because conducting polymer LEDs are easily patterned, operate at low DC voltages, and have uniform areas of light, there is a potential market for low level backlighting and alphanumeric displays.

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## BIOGRAPHIES



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