
CHAPTER 6

ELECTROPOLYMERIZATION

6.1 INTRODUCTION

Property of most polymers, which distinguishes them from metals, is their inability to carry electricity. In fact, the insulating properties of polymers are a significant advantage for many applications of plastics. Electrical wires, for example, are protected from shorting by a coating of insulating polymer. It is a general view that plastics and electrical conductivity are mutually exclusive. During the past 15 years, however, a new class of organic polymers has been devised with the remarkable ability to conduct electrical current. Part of a larger class of materials called "synthetic metals," some of these conductive plastics are already under development for practical applications, such as rechargeable batteries, electrolytic capacitors, and "smart windows" that absorb sunlight in summer. They are tremendous potential for future scientific and technological development. Excitement about these relatively new materials is high because a plethora of new, often exotic, applications may materialise. The novel materials that can be fabricated into electrical wires, and other shapes is fascinating and brought together scientists from traditionally different areas, such as chemistry, physics, electrical engineering, and materials science, to work toward a common goal: controlling the electrical and mechanical properties of these materials. As a result, work in the field of conductive polymers is highly interdisciplinary. A major obstacle to the rapid development of conductive polymers is the lack of understanding of how electrical current passes through them. All conductive polymers have one thing in common: They contain extended π -conjugated systems—single and double bonds alternating along the polymers chain. A basic research goal in this field is to understand the relationship between the chemical structure of the repeating unit of the polymer and its electrical properties. Such an understanding would enable the electronic and mechanical properties of these materials to be tailored at the molecular level.

Simple band theory fails to explain conductivity in polymers. The electrical properties of any material are determined by its electronic structure. The theory that most reasonably explains the electronic structure of materials is band theory. In the solid state, the atomic orbitales of each atom overlap with the same orbitales of their neighbouring atoms in all directions to produce molecular orbitales similar to those in small molecules. In a solid, the number of atomic orbitales is about 10^{22} per cc, and thus the number of molecular orbitales would also be 10^{22} . When this many orbitales are spaced together in a given range of energies, they form what looks like continuous energy bands.

How many electrons these bands have and where the highest occupied and lowest unoccupied bands are depends on how many electrons the original atomic orbitales contain and the energies of the orbitales. The energy spacing between the highest occupied lowest uncoupled bands is called the band gap. The highest occupied band is called the valance band, and the lowest unoccupied band is the conduction band.

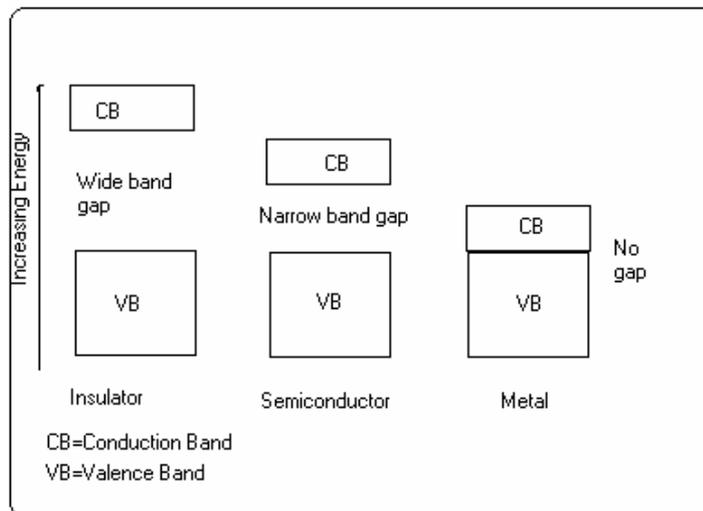
The electrical properties of conventional materials depend on how the bands are filled. When the bands are filled or empty, no conduction occurs. If the band gap is

narrow, at room temperature thermal excitation of electrons from the valance band to the conduction band gives rise to conductivity. This is what happens in classical semiconductors. When the band gap is too wide, thermal excitation at room temperature is insufficient to excite electrons across the gap and become an insulator. The high conductivity of metals is due to partially occupied bands- a partially filled conduction band, a partially empty valance band, or a zero band gap.

Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Their electrical conductivity cannot be explained well by simple band theory. For example, simple band theory cannot explain why the charge carriers, usually electrons or holes, in polyacetylene and polypyrrole are spinless. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons, and bipolarons, have been applied to conducting polymers since the early 1980s.

When an electron is removed from the top of the valance band of a conjugated polymer, such as polyacetylene or polypyrrole, a vacancy (hole or radical cation) is created that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. The energy level associated with this radical cation represents a destabilised bonding orbital and thus has a higher energy than the energies in the valance band. In other words, its energy is in the band gap. This rise in energy is similar to the rise in energy that takes place after an electron is removed from a filled bonding molecular orbital.

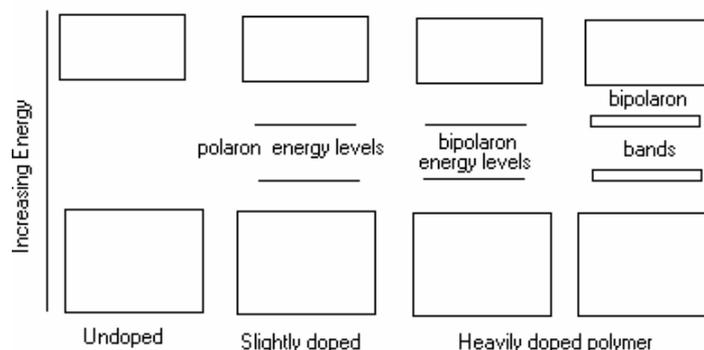
In solid-state physics, a radical cation that is partially delocalized over some polymer segment is called a polaron. It stabilises itself by polarizing the medium around it hence the name.



In polypyrrole low doping concentrations create paramagnetic polarons, which, as the degree of doping increases, convert to spinless bipolarons, which extend over about four pyrrole rings. A polaron and bipolaron in polypyrrole are shown below:

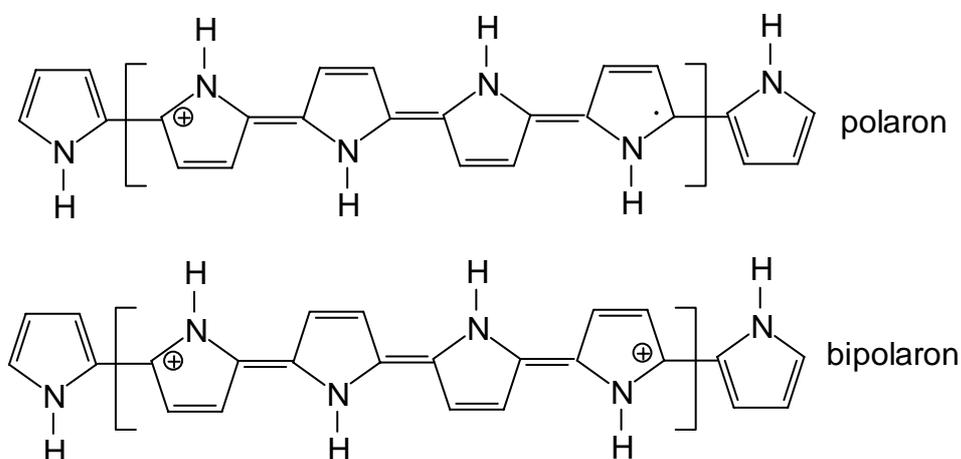
In the polymer, the pyrrole units have positive charges, which are balanced by a variety of so-called dopant anions. Anions are expelled from the polymer film (undoping) when a negative potential is applied to the films, thus reducing it to the

neutral state. Conversely, when positive potential is applied to oxidize the neutral film (doping), anions are taken up.



During the doping-undoping process, the volume of the film changes as much as 50 %, depending on the specific volume of the dopand anion. Also, dramatic color changes occur because the visible spectra of the doped and undoped film are very different. In the undoped state, polypyrrole is neutral with greenish but transparent coloration. When doped, it becomes opaque and extremely absorbing in practically all wavelengths, but with characteristic broad absorption maxima.

The heterocyclic polymers can be prepared either chemically or electrochemically. For example the polypyrroles prepared via the two routes have different physical appearances. The chemical oxidation method usually leads to fine polypyrrole powders, while the electrochemical synthesis provides freestanding polypyrrole films. The resulting conductivity is generally higher is the latter method.



However the size, shape and nature of the electrode restrict the use of the electrochemical method involved, by the brittleness of the obtained films and by the difficulty in preparing thick films. The chemical route becomes, thus, the alternative choice for preparing large size conductive polymers.

6.2 EXPERIMENT

The conventional three-electrode system is used for electrochemical polymerization. The anode is a Pt disc (area= 0.2 cm²), the cathode is a Pt wire and the reference electrode is a saturated calomel electrode (SCE) connected to the measuring

solution by a Luggin capillary via a salt bridge. A Wenking POS 73 Model Scanning potentiostat is employed for the electrolysis. Polymer is formed as a film on the Pt electrode surface in CAN solution containing 0.1 M supporting electrolyte. Electrolysis potential is +1.2 V.

6.2.1 MATERIALS REQUIRED

Monomer (0.01 M) which can be successfully electropolymerized [Pyrrole (Py) thiophene (Th) aniline (An), N-carbazoles (N-vinyl carbazole (NVCz), carbazole (Cz), ethylcarbazole (ECz)], Solvent usually are (10 ml) Acetonitrile (ACN), and dichloromethane (DCM). Supporting electrolyte 0.1 M [tetraethylammonium perchlorate (TEAP), tetraethylammonium hexafluoroborate (TEA PF₆), tetraethylammonium tetrafluoroborate (TEA BF₄)]

6.2.1.1 Apparatus

- An electrochemical cell
- A thermostat
- Electrodes (Working= (Pt wire), Counter=(Pt wire), Reference=Saturated Calomel
- Electrode (SCE))
- Fourier transform infrared (FT-IR) spectra (Mattson 1000 FT-IR spectrometer)
- All reactions will be followed monitoring between 200 and 1100 nm by using a UV-Visible spectrometer. (Shimadzu UV-160 A).
- Electrical conductivities of products will measure by using four-point probe technique.
- Cyclic voltametric experiments of monomers and polymers will accomplish with a Potentiostat Wenking POS 73 with Kipp and Zonen X-Y Recorder.

6.2.1.2 Preparation Of Electrodes

The Pt electrodes will be cleaned prior to each scan. Polishing of electrodes will performed using a diamond paste (0.5 μm) followed by rinsing with deionized water and methanol in an ultrasonic bath for 10s. The surface oxide will be removed by etching for 30 s in dilute HNO₃ and H₂SO₄ solutions followed by rinsing with deionized water and dried under vacuum.

6.3 CHARACTERISATIONS

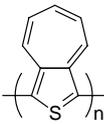
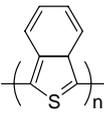
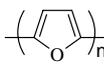
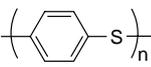
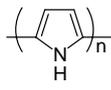
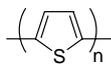
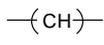
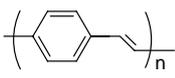
1. Collect the FT-IR spectra of products recorded on a FTIR spectrophotometer by KBr discs. Give the characteristics peaks of each polymer in a table.
2. Compare these polymer spectra with the spectra of each monomer.
3. Measure the electrical conductivities of the products by using four-point probe technique by polymer discs. Collect the results in a table.
4. Monitor the reactions of soluble part of polymers between 200 and 1100 nm by using a UV-Visible spectrophotometer.
5. Calculate the peak currents and potentials of monomers during the cyclic voltametric measurements and compare these values with the values obtained for polymers.
6. Plot the peak current, and potentials of monomers versus scan rate and cycle number. Compare the redox potentials of polymers with each others.
7. Calculate and compare the redox capacities of each polymer for three different supporting electrolytes.

REFERENCES

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3. *Handbook of conducting Polymers* Terje A Skotheim Marcel Dekker Inc. New York. (1986)
4. *Conductive Electroactive polymers Intelligent Materials Systems* Gordan 6. Wallace, Geoffrey M. Spinks, Peter R. Teasdale, Technomic Publishing Company 1997 USA

APPENDIX

Conductivities of conducting polymers.

Polymer	Structure	Doping Materials	Conductivity (Ohm ⁻¹ cm ⁻⁶)
PolyAzulene		BF ₄ ⁻ , ClO ₄ ⁻	1
Polyisothia-napthene		BF ₄ ⁻ , ClO ₄ ⁻	50
Polyfuran		BF ₄ ⁻ , ClO ₄ ⁻	100
Polyphenylene sulfide		AsF ₅	500
Polypyrrole		BF ₄ ⁻ , ClO ₄ ⁻ tosylate ^b	500-7500
Polythiophene		BF ₄ ⁻ , ClO ₄ ⁻ tosylate ^b	1000
Polyacetylene		I ₂ , Br ₂ , Li, Na, AsF ₅	10000 ^a
Polyphenylene-vinylene		AsF ₅	10000 ^a

^a Conductivity of oriented polymer, ^b p-Methylphenylsulfonate