THESIS ENTITLED

PREPARATION OF ORGANIC SEMICONDUCTORS INCLUDING OLIGOMERS AND CHELATED COMPOUNDS.

Submitted To

University College For Women

Ain-Shams University

For

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CHEMISTRY

By

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Thesis entitled

Preparation of organic semiconductors including oligomers and chelated compounds.

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Note

Beside the work carried out in this theis the candidate has attended post graduate courses for on year in organic chemistry covering the following topics.

1- Spectroscopy.

Instrumental analysis.

2- Organometallic compounds.

advanced chemical reaction.

3- Photochemistry

Quantum chem.

4- Thermodynamic

Chemical Kinetical.

5- Natural Products.

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Deo Gratias

C O N T E N T S

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AIM OF THE WORK

In recent years the discovery of highly conducting graphite intercalation compounds, (Vogel, 1977) graphite superconductivity, metallic polysulfur nitrogen (Kronick et al., 1962), and doped polyacetylenes that can be made to exhibit metallic conductivity as well as n-type or p-type semiconductivity(Shirakawa et al., 1978), means that the range of conductivity of carbon-based polymers can be regarded as covering a similar span. The purpose of this work is to discuss the electrical conductivity of some oligomers and chelated compound and see the most proper conditions of obtaining an organic compound which should have a higher conductivity in the range of semiconductors. This material could be used in constructing a solar cell, (E.Vander Donckt). It will be of greater value and high interest if the construction of this cell would be economic and having a high efficiency. In this work we did not construct the solar cell. However we could prepare oligomers that have considerable conductivity in the range of semiconductors. Thus and according to Vander Donckt method, the construction of a solar cell containing one of these organic materials as one of its constituents, became an easy task. By means of this cell Vander Doncket et al. could change the light energy into electric energy. The conversion efficiency of white light into electricity was 5×10^{-2} %.

INTRODUCTION

Photochemistry is the branch of chemistry that deals with the processes following the absorption of a photon of electromagnetic radiation by a molecule [1]. When the absorbed photon is in the visible or ultraviolet region of the spectrum, the absorbed energy results in an electronically excited species. Processes resulting in a permanent chemical alteration of a molecule or its chemical reaction with another molecule are called photochemical processes. One of the many possible photoelectric processes is one that leads to a separation of electrical charge or ion, thus producing a positive (hole) or negative (electron) species. If either of these charges or ions is able to migrate under the influence of an electric field, electrical conductivity results and the material is said to be a photoconductor. The photoelectrical processes that can occur in small molecules may also occur in macromolecular systems. In addition extensive intramolecular energy migration and interactions between nearly groups is also possible in macromolecules.

1- Semiconductivity of simple organic molecules[2,3], protein molecules[4], chelated molecules[5,6] and also of dyestaffs[7] were studied before. Klopifer[8,9, 10]

CHAPTER I

I N T R O D U C T I O N

and Okamoto[11,12] studied the photoconductivity of poly-N-vinylcarbazole. The main purpose of these authors was to obtain an organic semiconducting material. The semiconductivity of other polymers such as poly-2-vinyl-pyridine was also studied, e.g., reference[13]. Vander et al. also constructed a solar cell from poly-2-vinylpyridine.

An electronically excited molecule may undergo any of numerous photochemical reactions including:

1. Bond rupture forming free radical fragments.
2. Intramolecular rearrangements.
3. Oxidation leading to ketone, aldehyde and peroxide groups, etc...
4. Moreover in polymer molecules depolymerization or unzipping following the formation of a free-radical fragments. Once a free-radical is formed on the main chain, the polymer will split off as a monomer, unit by unit, and continue to depolymerize to a monomer. The ceiling temperature is the temperature above which the equilibrium between the monomer and polymer lies in the direction of the monomer . The presence of small amount (traces) of an electrolyte or small molecules increases the electric conductivity of the material[14,15], (e.g. a polymer or a chelated compound). The explanation of this behaviour is that the traces of the substance introduced acts as

an electron donor or an electron acceptor. This phenomenon leads to the generation of charged particles or free radicals. As an example if D is the host material, which may be an electron donor, doped with traces of a substance which acts as an electron acceptor A then we would have

$$DA \xrightarrow{\text{heat or light}} D^{+} A^{-}$$

In the case of examining the material, whether it is diamagnetic or paramagnetic, an electric field (a polarizing electric field), is applied and pass through the material. The existing potential gradient assists in the generation, separation and migration of the charged carrier species produced by excitation of light(or heat), where the externally applied field are required to produce current. Normally, in the absence of such an applied field, photogenerated species in a photoconductor simply recombine, leading to current decay. Thus the procedure involved in finding a photoconductor that will be a good photovoltaic material necessitates the presence of four steps :

1. Photogeneration of charged or neutral carrier species,
2. Charge separation or generation from neutral carrier species,
3. Charge transport, and
4. Charge collection to yield current.

The increase in conduction originates from an increase in the concentration of charge carriers upon the absorption of photons. Excitation may be also by other methods, as temperature or γ-rays.

In order that any material to be considered as a semiconductor, (a paramagnetic material) it must have the following properties:

1. Its electric resistivity should be in the range of 10^{+7} to 10^{-3} ohm^{-1}.cm^{-1}.
2. It should give a straight line when the logarithm of its electric resistivity is plotted versus I/T, where T is the absolute temperature. The slope of this straight line shows the activation energy for electric conductivity.
3. Paramagnetic behavior is observed when one or more of the subgroups of electrons is incomplete[16,17], and hence it is to be expected in molecules and ions with an odd number of electrons. The magnetic permeability, μ of a medium is a measure of the tendency of the magnetic lines of force to pass through the medium in comparison with a vacuum or air. For a paramagnetic substance, μ is slightly greater than unity while for diamagnetic substance $\mu < 1$. For ferromagnetic substances μ is highly greater than 1, i.e. $\mu \gg 1$. From magnetism we have the relation:

$$B = 4\pi I + H$$

Where B is called the magnetic induction. It depends on the strength of magnetic field and on the type of the material, i.e., diamagnetic, paramagnetic or ferromagnetic. I is the induced magnetization and H is the magnetic field.

The upper mentioned relation is also written:

$$u H = 4\pi I + H$$

I = kH, where k is called the susceptibility so:

$$u = I + 4\pi k$$

k could be determined experimentally by E S R measurement.

In the case of paramagnetic substances, the E S R spectrum show sharp peaks due to hyperfine splitting which indicate that the substance is in the triplet state. Molecules with all electrons in paried spine states ($\uparrow\downarrow$) are said to be in a singlet state, while those with two unpaired electrons ($\uparrow\uparrow$) are called triplets. Simply the appearance of sharp hyperfine splitting of the E S R spectrum indicates the presence of single or unpaired electrons. In the case of paramagnetic atoms the orientation of magnetic moments takes place in the direction of the magnetic induction. Otherwise the magnetic susceptibility of a substance is measured by the difference in its weight in air or vacuum and in a magnetic field.