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Conducting Polymers and Their Applications in Sensors: A review

Samia Mezhr Merdas*, Auhood kadhim zaid*, Zainab M. kareem*

*Department of Chemistry, College of Science, University of Thi-Qar, Iraq

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Abstract:

Conducting polymers (CPs) have drawn considerable attention because of their economical importance, good environmental stability and electrical conductivity as well as due to their useful mechanical, optical and electronic properties. The present review describes the salient features of conducting polymers as biosensors and chemical sensors (Thermal sensors, Mass sensors, Electrochemical sensors, Optical sensors), their concepts, construction, working, types importance and applications.

Keywords: Biosensors, Electrochemical sensors, Chemical Sensors Conducting polymers, conjugated polymers

1. Conducting polymers:

Conducting polymers (CPs) are recognized as a class of organic materials with unique optical and electrical properties similar to those of metals and inorganic semiconductors [1-2]. Over the last decade, CPs have received enormous interest over the last decade resulting to an explosion of publications. The research in this area has provided the fundamental understanding of the physics, chemistry and material science of these materials and has supported the industrial growth of CPs products [3-10]. CPs can be synthesized using versatile, simple, and cost-effective approaches. They can be easily assembled into supramolecular structures with multifunctional capabilities by using simple electropolymerization processes [1-2]. Various kinds of conducting polymers have been produced and are widely in use due to reasonably high conductivity, as recorded in Figure.1. CPs are commonly polyconjugated structures, which are insulators in the pure state but when treated with a reducing or oxidizing agent can be converted into polymer salts with electrical conductivities comparable to metals. Conjugated polymers in their non-doped state are in fact intrinsic semiconductors whose band gap depends not only on the chemical constitution of the conjugated backbone (Figure 2.) but also on the nature of the substituent's attached to the main chain. Thus electronic and optical properties of the conjugated polymers can be greatly varied extent by appropriate functionalization. Like the Conducting polymers, the semi-conductive polymers obtain their properties from their valence molecular orbitals and conduction-molecular orbitals, i.e., antibonding π^* and orbitals bonding π , respectively.

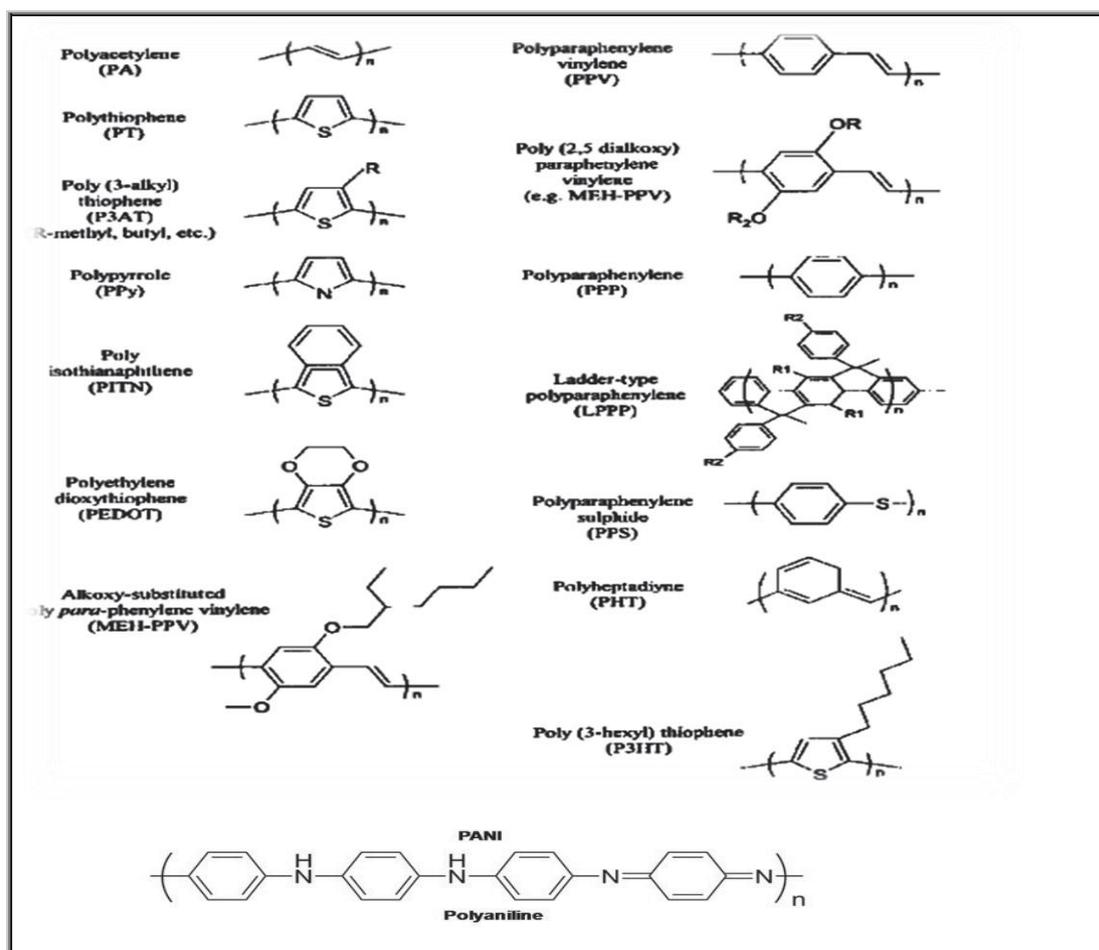


Figure1. Structure of some conducting polymers [10]

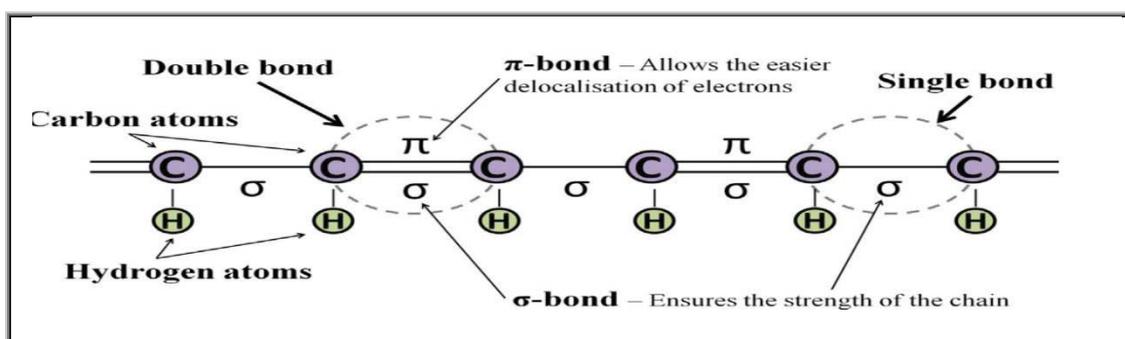


Figure. 2. A simplified schematic of a conjugated backbone: a chain containing alternating single and double bonds [11].

In electro-chemical light emitting cells, the semi-conductive polymer could be surrounded asymmetrically with a hole-injection electrode on one side, and a low work function, electron injecting metal contact like calcium magnesium, aluminum etc. on the other side. The emission of light is then the result of radiative charge carrier recombination in the polymer as electrons from one side and holes from the other recombine. CPs are conjugated polymers, namely organic compounds that have an extended p-orbital system, through which electrons can move from one end of the polymer to the other. The bonding in conjugated polymers leads to one unpaired electron (the π -electron) per carbon atom. Moreover, π -bonding, in which the carbon orbitals are in the sp^2 p_z configuration and in which the orbitals of successive carbon atoms along the

backbone overlap, leads to electron delocalization along the backbone of the polymer. This electronic delocalization provides the “highway” for charge mobility along the backbone of the polymer chain. Electronically conducting polymers are extensively conjugated molecules. Also it is believed that they possess a spatially delocalized band-like electronic structure. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors [10].

3. History of Conducting polymers:

Conducting polymers are a class of new materials that have electronic conductivity. The discovery of polymers with high conductivity has led to a new and exciting area of material science [12,13]. Polyacetylene was the first polymer that could be made electronically conductive [14]. The first experiments were made in the mid-1970s, and since then a number of other conducting polymers have been synthesised. The most important polymers are polyacetylene [14-16], polypyrrole [17], polythiophene [18], polyaniline [19], polyphenylene [20] and poly (phenylene vinylidene) [21]. These polymers are characterised by electronic conductivities of up to 10^4 s cm^{-1} . Conducting polymers can be prepared either by chemical or electrochemical. Conducting polymers can be prepared either by chemical or electrochemical polymerisation from a monomer solution containing an electrolyte salt. The electrochemical method is especially attractive [22], since the oxidation of a monomer solution in appropriate conditions gives a doped film deposited at the surface of the electrode and enables good control of growth rate and film thickness to be achieved in addition, the electrochemical method allows the oxidation potential of polymerisation to be controlled and thus the quality of polymer can be optimised. Electrochemically synthesised polymer films also have adequate mechanical properties compared to chemical methods. For electrochemical polymerisation, a three-electrode voltammetric cell is normally used. The working electrode on which the polymer film is formed is of importance. Since polymer films are obtained at positive potentials, the electrode material should not oxidize concurrently [23]. Usually, the working electrode is made of platinum [24,25], gold [26], glassy carbon [27,28], or ITO (indium-tin oxide) coated glass [29]. The auxiliary electrode can be made of platinum gauze or reticulated vitreous carbon [30,31]. The reference electrode can be Ag/AgC or SCE used in aqueous solution, while in organic solvents the Ag/Ag reference electrode is usually employed [30-33]. The electrochemical preparation of conducting polymers dates back to the early work of Dall'Olio and co-workers [34], who obtained the powdery, insoluble precipitate "pyrrole black" on a platinum electrode by electrochemical oxidation of pyrrole in aqueous sulphuric acid. Then, Diaz et al. reported the electrode position of a free standing, coherent and highly conducting polypyrrole film from an organic medium [35]. Since then, other Conductng polymers such as polythmophene, polyfuran, polyindole and pelyazulene were prepared using electrocihematical methods [36]. Among them, polypyrrole has been intensively studied [37-39] due to the fact that the polypyrrole system is quite attractive as an electrode material because of its chemical and thermal stability and the ease of preparation of derivatives having a range of conductivities. Polymer properties like morphology, electroactivity and conductivity are very much dependent on the polymerisation conditions used including the monomer concentration, solvent, electrolyte, temperature, and the potential current applied [23, 30]

4. Sensors:

Sensor is a device that when exposed to a physical phenomenon (temperature, displacement, force, etc. produces a proportional output signal (electrical, mechanical, magnetic, etc.)[40,41]. The term transducer

is often used synonymously with sensors. However, ideally, a sensor is a device that responds to a change in the physical phenomenon. On the other hand, a transducer is a device that converts one form of energy into another form of energy. Sensors are transducers when they sense one form of energy input and output in a different form of energy. For example, a thermocouple responds to a temperature change (thermal energy) and outputs a proportional change in electromotive force (electrical energy). Therefore, a thermocouple can be called a sensor and or transducer. Many measuring and sensing devices, as well as loudspeakers, thermocouples. Microphones, and phonograph pickups, may be termed transducers. Systems of sensors and transducers are constructed for a variety of applications including surveillance, Imaging, mapping and target tracking in some cases, the sensors provide their own source of illumination and are referred to as active sensors. Passive sensors, on the other hand, do not provide illumination and depend on variations of natural conditions for detection. Conducting polymers have been widely explored as chemical sensors, optical sensors and biosensors because their electrical and optical properties can be reversible changed by doping/depoining processes [42–46].

4.1. Chemical Sensors:

A chemical sensor is a transducer which provides direct information about the chemical composition of its environment It consists of a physical transducer and a chemically selective layer [47]. Chemical sensors are defined by TUPAC as devices that transform chemical information into analytically useful signals [48]. Basically, a typical chemical sensor consists of two critical units: the receptor unit and the transducer. The receptor unit possesses a recognition process which transforms the information from chemical interactions into an appropriate form of energy that subsequently can be measured with the transducer. Alternatively, the transducer unit transforms the energy carrying the chemical information of the sample analyte into a useful analytical response due to the differences between recognition processes as well as signal transduction, chemical sensors can be greatly different from one to another according to the types of operation mechanism of transduction, chemical sensors may be divided into four modes: thermal, mass, electrochemical and optical.

(a) Thermal sensors:

Heat is a general property of any chemical reaction, as such is should be an ideal physical parameter to use for sensing. Unfortunately, its flow is difficult to control. The partial solution for the heat management in any integrated chemical sensor has been suggested [49]. Enzymatic reactions act as chemically selective heat generators. The thermistor appears to be the most popular temperature-sensing probe because of its cost, availability stability and sensitivity. For this reason, almost all thermal Sensors rely on enzymes for the selectivity. The first integrated thermal sensor for glucose using the temperature dependence the output of the Darlington amplifier has been constructed [50].

(b) Mass sensors:

The measurement of the change of mass as the means of chemical sensing is almost as universal as is the measurement of reaction heat. In principle it is applicable to any reactions in which there is a net change of mass. There are two types of mass chemical sensors. The first type is those based on piezoelectric bulk oscillators in which quartz crystal microbalance (QCM) is the most common material used for the bulk Oscillators, but other materials, such as poly (vinyl fluoridone) (PVF) [51] and ZnO [52] can also be used. The second type are those based on surface acoustic wave (SAW) devices.

(c) Electrochemical sensors:

This kind of sensors constitutes the largest group of chemical sensors. In electrochemical sensors the response is derived from the interaction between chemistry and electricity. Based on the modes of measurement of electric parameters, three main types of sensors can be categorized, i.e. potentiometric sensors on the measurement of cell voltage derived from the work of Nernst sensors on the measurement of cell current derived from the work of Heyrovsky(S), and conductometric sensors on the measurement of cell admittance derived from the work of Cavendish [53].

(d) Optical sensors:

This relies on the intrinsic optical property of the analyze. More and more enthusiasm has been attracted in the recent years for optical sensors [47] due to the fact that most of the optical hardware developed primarily for communication purposes can be readily adopted for chemical sensing as well as their high suitability for remote (kilometers) sensing and the safety of their operation.

4. 2. Biosensors:

A biosensor is an analytical device which combines a biorecognition element with a transducer [54]. While the biorecognition element determines the degree of selectivity or specificity of the biosensor, the biosensor's ability to detect low concentrations is mainly influenced by the transducer, as it transforms the biological or biochemical response into a quantifiable output signal [55]. Biosensors can be classified by the transduction principle, i.e., the detection, or by the type of the biorecognition layer which defines the type of specific analyte binding [54]. Table 1 gives an overview of the most common types of biosensors following these classifications. It is obvious that, for instance, immune sensors can be designed using optical or electrochemical detectors, acoustic biosensors can be based on antibody or aptamer coating, et cetera. Terms such as "micromachined" biosensors are sometimes used to describe the manufacturing method and therefore may include several types of biosensors, regardless of the transduction or biorecognition principle [56].

Table 1: Classification of biosensors

biosensors by transduction principle	biosensors by biorecognition element → alternative biosensor term* (if available)
Electrochemical	enzyme → enzyme sensor
Optical	antibody → immunosensor
Acoustic or gravimetric	aptamer → aptasensor
Thermal or calorimetric	oligonucleotide → DNA sensor, genosensor
Magnetic	cell → whole (microbial) cell biosensor molecular imprinted polymer

*instead of [biorecognition element] biosensor

5. Applications Conducting polymers in Sensors:

Conductive polymers have also considered potential materials as sensors because of their inherent optical, electronic and mechanical transduction mechanisms [57]. These sensors have advantages such as relative low cost, reversible signal transduction, high sensitivities and rapid response at room temperature

[58]. Gas sensors have a broad range of applications such as industrial production, food processing, environmental monitoring, health care, etc. [59–61]. The polyaniline (PANI) nanofibers synthesized by interfacial polymerization have shown that they have much higher sensitivity for the detection of NH_3 than conventional PANI films [62]. On the other hand, the addition of a second component into 1D-nanostructured conducting polymers can enhance their applications as gas sensors [63]. Besides NH_3 , the addition of metal oxide nanoparticles into 1D-nanostructured conducting polymers can extend their applications in detecting other gases. For example, PANI/ In_2O_3 composite nanofibers synthesized via chemical polymerization were used as sensors in detection of H_2 , CO and NO_2 at room temperature [64]. PANI/ WO_3 composite nanofibers were also employed in sensors for detection of H_2 gas; however, the sensitivity was worse than PANI/ In_2O_3 composite nanofiber-based sensors [68]. Metal salts can also be incorporated into the 1D-nanostructured conducting polymer matrix as gas sensors. For example, PANI/ CuCl_2 composite nanofibers exhibited a high response for H_2S gas [66]. PANI-PVP blend has improved sensitivity towards CHCl_3 and least sensitivity towards CH_2Cl_2 [67]. The polypyrrole – chitosan layer has been used to detect Zn^{2+} and Ni^{2+} ions in aqueous solution by surface plasmon resonance [68]. Electrospun PEDOT: PSS (PEDOT–poly(styrenesulfonate))-PVP (polyvinyl pyrrolidone) blend nanofibers showed good reversibility and reproducibility in organic vapor sensing, and the conductivity value for PEDOT: PSS-PVP nanofibers was 2.34×10^{-12} S/cm [69]. Compared with PVP nanofibers, PEDOT: PSS/PVP nanofibers exhibited better organic vapor sensing performances to ethanol, methanol, THF and acetone [69]. Electrospun nanofibers have been confirmed to be good candidates for ultra-sensitive gas sensors due to the improved surface area-to-volume ratios of coatings [70]. Higher surface area led to higher sensitivity and fast response time [70]. PANI nanofibers with some beads and a small content of PEO revealed high sensitivity, fast response and small hysteresis because beads could help to improve adhesion to the electrode (which enhances electrical contact and sensing ability), and PEO helped to increase the hydrophilicity of the PANI nanofibers, and humidity responses [71]. PANI-polyvinyl pyrrolidone (PVP) composite fibers were prepared for NO_2 sensing and these mats were reported as a good candidate for this application [72]. PANI-nylon-6 blend nanofiber mats were prepared for determining organic compounds with the advantages of good sensitivity and reproducibility [73]. PANI coated PMMA nanofibers were also used for gas sensing [74]. Electrochemical capacity due to high doping levels and ease of charge transfers reactions. In their study, a PPy composite nanofiber electrode was compared with the electrode film that was produced by a casting method. Electrospun PPy-sulfonated-SEBS fibers were called E-PSS, electrospun PPy-SEBS fibers were called E-PS. PPy/SEBS (C-PS) was prepared by the casting method [75]. In another study, nano-structured PANI was tested for sensor, actuator, supercapacitor and gas-separation membrane applications [71]. PAN-PPy-based electrodes were prepared and these mats show good cycling performance with high reversible capacity [76]. Pringsheim et al. [77] reported that fluorescent beads coated with polyaniline can be used as a novel optical pH sensor. Gu et al. [78,79] demonstrated a single wave-guiding polyaniline-polystyrene nanowire for highly selective optical detection of gas mixtures. Wang et al. [80,81] investigated the photosensitivity and photoresponse of a bundle of polyaniline nanowires, which showed that the conducting polymer nanofiber might be useful in the fabrication of photosensor and photoswitch nanodevices. Zhu et al. [82,83] reported a pH sensor of polyaniline perfluoro sebacic acid-coated fabric. Recently, conducting polymers have attracted much interest in the development of biosensors because they act as excellent materials for immobilization of biomolecules and rapid electron transfer for the fabrication of efficient biosensors [84]. Detection of H_2O_2 is important because it is often a product in enzymatic reactions. PANI/PS composite nanofibers prepared by electrospinning technique were employed to detect H_2O_2 [85,86]. Composite nanofibers containing

PANI, Fe₃O₄ and CNTs were prepared and doped with enzyme for the fabrication of glucose biosensors [87]. Conducting polymer nanocomposites, when encapsulated with lipase, can be utilized as biosensors to detect triglyceride [88]. Shin et al. fabricated an amperometric cholesterol biosensor using polyaniline-coated polyester films for the detection of triglycerides [89]. Immobilization of DNA onto conducting polymers has been extensively studied for detection of various DNA target sequences and microorganisms [90,91] Zhang et al. [92] reported poly (methylvinyl etheralt-maleic acid)-doped polyaniline nanotubes for oligonucleotide sensors. Peng et al. [93] reported a functionalized polythiophene as an active substrate for a label-free electrochemical geno-sensor. Langer et al. [94] reported a bacterial nanobiodetector, which can also be utilized in bio-alarm systems.

6. Conclusion:

In this review a comprehensive overview of conducting polymers and their advantages and applications in sensors, were fully discussed. On one hand, Conductive polymers (CPs) for sensors present numerous advantages such as high sensitivity, short response time, room temperature operation, and the possibility of tuning both chemical and physical properties by using different substituents. And on the other hand, the realization of applying these sensors in real life will take a long time and needs more effort from researchers from all over the world.

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