The Conducting Bological Pigment; Melanin Polymer

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ABSTRACT: This article reviews about naturally occurring conducting polymer, Melanin. In this paper detailed explanation was included conducting polymers that have been developed with wide range of properties and potential applications due to their chemical, mechanical, optical and electrical properties such as sensors, electromechanical devices, batteries and electro chemical cell. In addition ist was also describer about Melanins that is serve as a free radical scavengers, antioxidants and photoconductors. However, some researchers have shown that cells containing small amount of melanin are more susceptible to damage from irradiation. This observation has been linked to iron content of melanin, in that when melanin is saturated with transition metal ions like iron it may actually produce free radicals and therefore accelerates cell death rather than protecting it. Therefore it is advisable to protect the melanin pigment from saturation with such transition metal ions (abstact).

Keywords : Melanin; Conducting polymers; Eumelanin; polymerization; (keywords)

1. Introduction

Traditionally polymers have been associated with insulating properties in the electronic industry and are applied as insulators of metallic conductors or photoresists. Since the discovery in 1977 of the doping of polyacetylene (PA), which resulted in increasing the conductivity of polyacetylene by eleven orders of magnitude, many academic and industrial Research laboratories initiated projects in the field of conducting polymers [1]. The importance of the field of semi conducting polymers was recently stressed by awarding the 2000 Nobel Prize in chemistry to the discoverers Heeger, Shirakawa and MacDiarmid [2]. The three winners established that polymer plastics can be made to conduct electricity if alternating single and double bonds link their carbon atoms, and electrons are either removed through oxidation or introduced through reduction. Normally the electrons in the bonds remain localized and cannot carry an electric current, but when “doped" with strong electron acceptors such as iodine, the polymer began to conduct nearly as well as a semi metal [1, 2]. Conducting polymers are conjugated polymers possessing an extended π - system and highly delocalized electronic states. This extended electron conjugation is what gives rise to their conductivity. However, unlike inorganic semiconductors (atomic solids), conducting polymers are typically amorphous polymeric materials and therefore charge transport in conducting polymers can be quite different from conventional semiconductors. The polymers themselves are not new; many of them such as polypyrrole are well known in their non conducting form before their conductivity was discovered. Indeed, it may be said that the discovery of conducting polymers is not the discovery of the polymer rather of its unique properties [3]. Nowadays, many different conducting polymers have been developed with wide range of properties and potential applications. Such classes of conducting polymers include polythiophene, polyfuran, polypyrrole, poly (*p*-phenylene), poly (*p*-phenylenevinylene), polyfluorene and polyaniline (PAN) **(** fig.1.1**)**. Although none have exhibited higher conductivity than polyacetylene, these polymers have been useful in designing new structures that are stable and soluble in some cases [3].

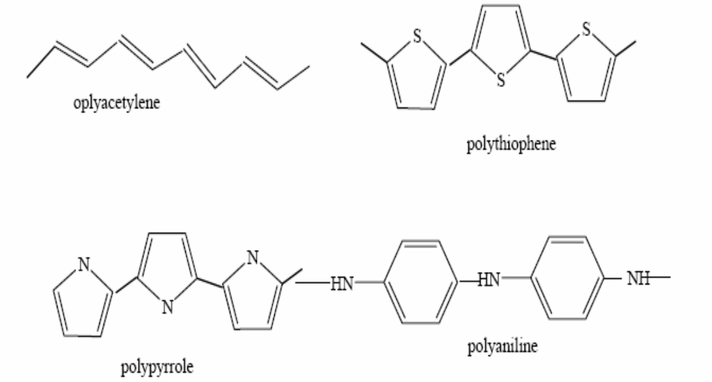


Fig 1.1 some of the well-studied conducting polymers [3].

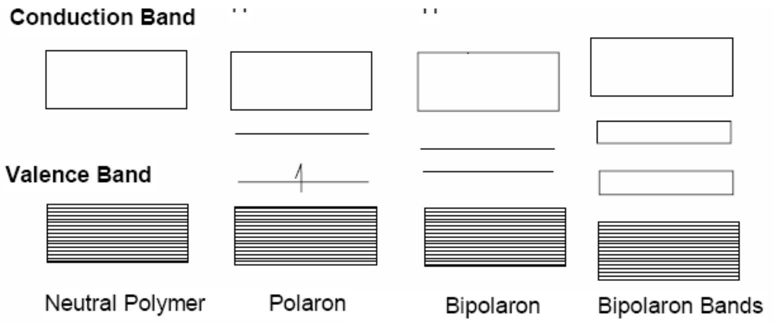
Polyacetylene was the first discovered and most well studied conducting polymer. However**,** since polyacetylene exhibits a very high conductivity in the doped form, the material is not stable against oxygen or humidity and is intractable. For these reasons, much work has been devoted to synthesizing soluble and stable polyacetylenes. Unfortunately, these substituted derivatives exhibit electrical conductivities that are much lower than that of the parent polyacetylene. The discovery of polyacetylene lead to the search for new structures that could lead to new improved polymer properties and these polymers have been useful in designing new structures that are stable and soluble in some cases [1, 3].

1.1 Doping of conducting polymers

The concept of doping is the unique, central theme which distinguishes conducting polymers from all other polymers. It must be noted that doping in conducting polymers is different from doping in conventional inorganic semiconductors in that it is purely redox process. The dopant counter ion is therefore incorporated to balance the charges created during doping and does not create the charge carriers itself [3]. There are two types of redox doping: anionic and cationic doping. Anionic doping occurs when the polymer is oxidized; creating a positive charge and therefore a dopant anion is incorporated to the polymer matrix to balance the charges. It is termed as a p-type of doping. Cationic or n-type of doping on the other hand occurs when the polymer is reduced and dopant cation is incorporated into the polymer matrix. Most hetrocycles such as polypyrrole and polythiophenes are susceptible to p-type doping, but some conducting polymers like polyacetylene or poly (para-phenylene) are susceptible to both types of doping [3]. A non-redox doping exists in some special cases where the number of electrons associated with the polymer back bone does not change. This can be observed in polyaniline where its emeralidine base can be treated with protonic acids to gain 9-10 orders of magnitude increase in conductivity. Doping can occur chemically or electrochemically. Chemical doping is achieved by using a suitable oxidizing or reducing agent in solution, while electrochemical doping is achieved by applying a suitable electrical potential to the polymer in a suitable electrolyte solution. Chemical doping has the benefit of being simple and straightforward process; however it can be difficult to control when one tries to obtain an intermediate doping level. Electrochemical doping, on the other hand, is usually applicable only to solid films, but the doping level in it can be precisely controlled by controlling the potential applied to the polymer. It is often part of electrochemical synthetic process of conducting polymers since their oxidation is lower than that of the monomer; hence the conducting polymer is synthesized in its oxidized conducting form [3]. Since dopant counter ions are incorporated in the polymer in significant amounts it plays an important part in determining the properties of the polymer. These are generally incorporated to conducting polymers during the synthesis; however they may also be incorporated later through chemical or electrochemical means. The nature of the dopant varies depending on the desired properties of the polymer [3].

1.2 Electronic Conduction in Conjugated Polymers

The electronic and optical properties of π-conjugated polymers result from a limited number of states around the highest occupied and the lowest unoccupied levels. According to the band theory, the highest occupied band, which originates from the highest occupied molecular orbital (HOMO) of each monomer unit, is referred to as the valance band (VB) and the corresponding lowest unoccupied band, originating from the lowest unoccupied molecular orbital (LUMO) of monomer is known as the conduction band (CB). The energy distance between these two bands is defined as the band gap (E_g), and in neutral conjugated polymers refers to the onset energy of the π-π* transition. The E_g of conjugated polymers can be approximated from the onset of the π-π* transition in the UV-Vis spectrum. Conjugated polymers behave as semiconductors in their neutral state. However, upon oxidation (*p*-doping) or reduction (*n*-doping), the inter band transitions between VB and CB can decrease the effective band gap and thereby, resulting in the formation of charge carriers along the polymer [1]. The studies concerning the application of band theory to conjugated polymers were initially focused on polyacetylene. In neutral state the two resonance forms of polyacetylene are degenerate and on oxidation lead to the formation of solitons. The localized electronic state associated with the soliton is a non bonding state at an energy lying in the middle of the π-π* gap, between the bonding and anti bonding levels of the polymer chain. The soliton is a defect both topological and mobile because of the translational symmetry of the chain. Soliton model was first proposed for degenerated conducting polymers (PA in particular) and it was noted for it's extremely one dimensional character, each soliton being confined to one polymer chain. Thus, there was no conduction via inter chain hopping. Furthermore, solitons are very susceptible to disorder, and any defect such as impurities, twists, chain ends or cross links will localize them. The application of an oxidizing potential to aromatic polymers with no degenerate ground states, destabilizes the VB, raising the energy of the orbital to a region between the VB and CB. Removal of an electron from the destabilized orbital results in a radical cation or polaron. Further oxidation results in the formation of dications or bipolarons, dispersed over a number of rings. These radical cations are the charge carriers responsible for conductivity in conjugated polymers. Because of the non degenerate energy transitions of conjugated polymers, structural changes result and are based on the most backbone will localize them widely accepted mechanism for PPv as shown in (Fig. 1.2.) [1].



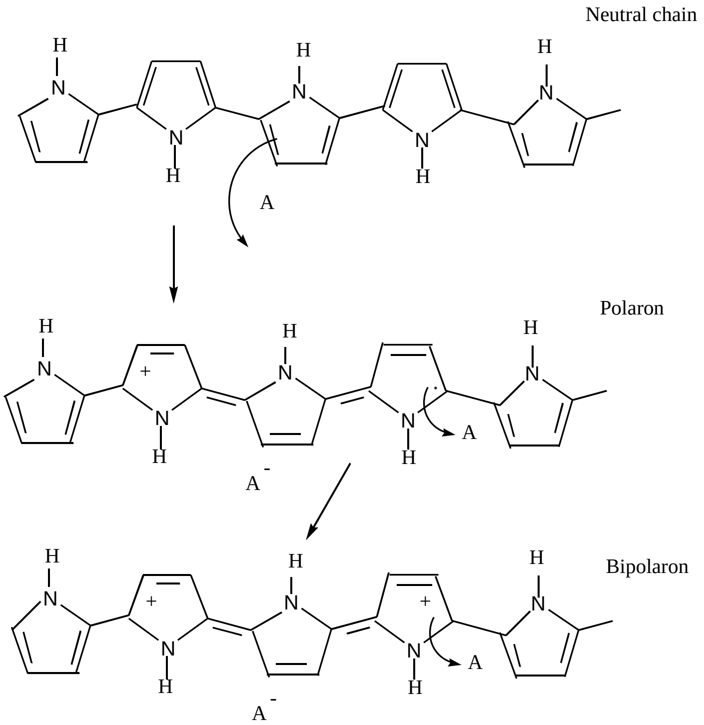


Fig.1.2 The transition between polaronic and bipolaronic states in polypyrrole [1].

1.3 . Potential application

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 eletrochromic devices (EDC's), rechargeable batteries, light emitting diodes (LED's), field effective transistors (FET's), photovoltaic cells and chemical Sensors [4]. Conducting polymers exhibit novel properties not typically available in other materials and these unique properties enable a large number of applications. These numerous applications can be split into three main classes. First, in their neutral form; using their semi-conducting and luminescent properties. Examples of applications that use neutral polymers are conjugated polymers as semi conducting materials for field effect transistors and as the active material in an electroluminescent device. The second category of applications involves using the polymer in its doped or conducting form, and some representative application in this category is electrostatic charge dissipation. The third category uses the ability of the polymer to reversibly switch between its conducting and reduced forms. Upon switching between these two states, the polymer undergoes color, conductivity, and volume changes [2]. The susceptibility of π-electrons of the conjugated polymers to oxidation or reduction alters the electrical, optical and electro optical properties of the polymers, since mostly the redox processes in the conjugated polymers are reversible. Therefore, the electrical and optical properties can be tuned systematically, with appreciable degree of precision by suitably controlling both the chemical or electrochemical oxidation and reduction. It is even possible to switch from a conducting to an insulating state and vice versa. Conducting polymers are thought to replace metals in future because they have superior properties such as ease of preparation, light weight and low-cost fabrication to metals which are also toxic and hazardous to the environment [1].

1.3.1 Sensors

Conducting polymers have attracted a lot of interest as a sensor material due to their properties being affected by their environment. The presence of certain gases, changes in humidity or other environmental variables can cause changes in the electrical properties. Greater selectivity and specificity can be achieved fictionalization of the polymer. The organic nature of conducting polymer means that various functional molecules can be incorporated in to the polymer either as a side chain or as a dopant. Changes in these functional molecules would be reflected as changes in the electrical or optical properties of the polymer. 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, selectivity, and sensitivity. Conducting polymers also change volume depending on their oxidation state. It is therefore possible for conducting polymers to convert electrical energy into mechanical work [3, 4].

1.3.2. Batteries

This field is the first area where conducting polymers promises to have a big commercial impact. Batteries have several key components: the electrodes allow for collection of current and transmission of power; the cathode material becomes reduced when the anode material is oxidized and vice versa; the electrolyte provides a physical separation between the cathode and the anode, and provides a source of cations and anions to balance the redox reactions. Aside from picking the best conducting polymer available, there are many other issues, not related to conducting polymers, which affect battery performance, such as electrolyte stability and stability of the counter half-cell reaction, and compatibility between the electrolyte and the materials. 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 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 polymers 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 [3, 4].

1.3.3. Electro chemical cell

These cells are used to go from opaque to transmissive at selected regions of the electromagnetic spectrum. Batteries and electro chemical cells have many common critical issues for commercial viability. They require cathodic and anodic reactions to be almost perfectly balanced (cyclic voltammetry is a good comparison tool for materials).The electrochromic window is similar to a battery with some additional requirements: at least one of the electrodes must be transparent to the given electromagnetic spectrum; the cathode material (which colors upon being oxidized) must be electrochemically reversible; the ion-conducting electrolyte must not only provide physical separation between cathode and anode, and possess a source of cations and anions to balance redox reactions, but must also be transparent to the given region of the spectrum; and the anode material (which colors upon being reduced) must also be electrochemically reversible [4]. The ion-conducting electrolyte in electrochromic cells is usually an inorganic salt dissolved in a solvent such as propylene carbonate with a polymer such as poly-(methyl methacrylate) added as a stiffener. The ion-conducting electrolyte acts as a source and sink for the ions as the various redox processes take place and maintains ionic contact between the materials. Conducting polymers also have an application in electrochromic cells, attenuating various regions of the electromagnetic spectrum. Many electrochromic cells need to last more than 10,000 cycles, and have switching times of a few minutes. In this case, spectroelectrochemistry is a good evaluation tool for conducting-polymer materials. Spectroelectrochemistry measures both the electrical and the optical response of the material in question. There is a great deal of data that indicates that conducting polymers are good candidates for materials in electrochromic cells. In particular, polythiopene, polypyrrole and polyaniline have been cycled more [4].

1.3.4. Radar Application

Radio Direction and Ranging (RADAR) uses electromagnetic waves that bounce off a particular target and are collected by

a receiver, which analyzes the signal and determines the range, direction, and speed of the object in question. Reflections occur whenever there is a sharp impedance difference between the medium (usually air) and the object. Impedance differences are most notable between metals and air. Metals tend to re-radiate (Reflect) the incoming signal [4].
Conducting-polymer camouflage works a little differently, in that it reflects back in a way that it has more continuously variable impedance. Microwave (100 MHz to 12 GHz) properties of conducting polymers have been studied, as have the millimeter wave (24 – 40 GHz) properties of polypyrrole-coated fibers. Conducting polymers as radar absorbers in antennas, Salisbury screens, camouflage, and other types of shielding are of interest to the military [4].

2. Melanin

2.1. Introduction

Melanins are naturally occurring biological pigments found in animals and plants. They may present in the skin, eyes, hair, feathers, scales and in the internal structures such as brain and inner ear as well as in the surface structures of vertebrates and are responsible for coloration in animals and some plants. There are two major classes of natural melanins, the black-brown eumelanin found in human black hair and in the retina of the eye and is nitrogen containing with higher molecular weight, and the yellow-red colored pheomelanin which is found in red hair and red feathers. Two biological functions of melanins have been identified. First, they have been shown to increase optical efficiency of the eye, and secondly, they are responsible for the production of color patterns in hair and superficial epidermis [5, 6]. Melanins are a class of functional biomacromolecules found throughout nature and possessing an intriguing and unique set of physical and chemical properties. In humans, they serve as our primary photoprotectant and pigment, and it has been recently suggested that they may be useful as high tech functional materials. The electrical behavior of melanin is highly dependent on its water content. Moreover, the dominant charge carrier within melanin does not appear to be electronic but something else which has a positive charge [7].

2.2. Melanin formation

Eumelanin is the more common form of melanins. It is derived from two chromophores, 5, 6-dihydroxyindole (DHI) and 5, 6-dihydroxyindole- 2-carboxylic acid (DHICA) (Fig. 2.1) in vivo by the enzymatic metabolism [7].

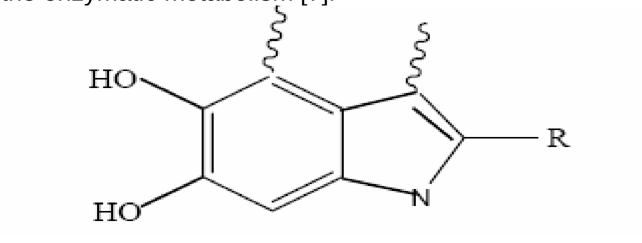


Figure 2.1: The monomer unit of eumelanin. The squiggly lines indicate attachment to other chromophores and possible proteins. The R group can be an H (for DHI) or COOH (for DHICA) [7]. These are formed from the oxidation of Tyrosine via the Raper-Mason scheme (Fig. 2.2) and go on to form melanin by a biosynthetic pathway known as melanogenesis. The overall molecular structure of eumelanin is considered to be a heterogeneous, chemically disordered substance derived from the indole units DHICA and DHI [7, 8].

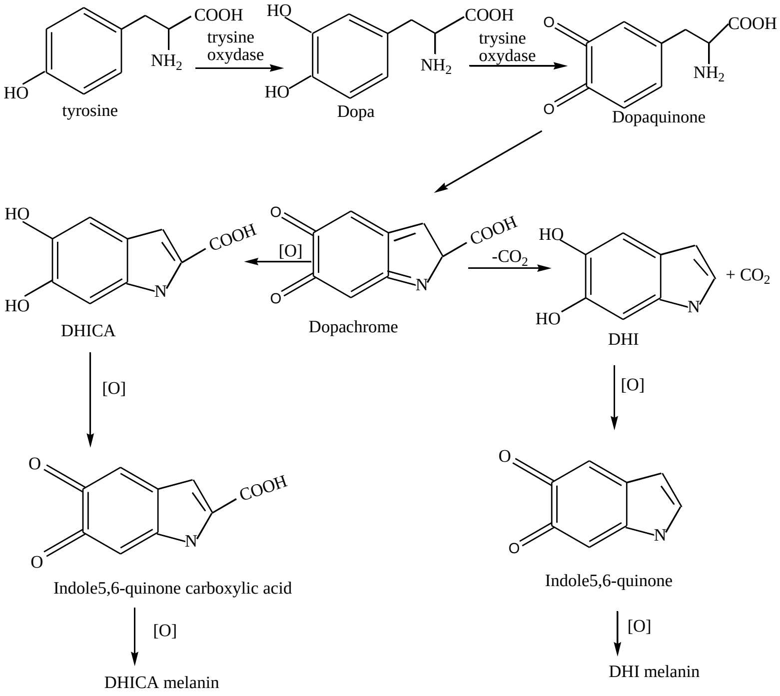


Figure 2.2: The Raper-Mason scheme of melanin synthesis *in vivo*. The reaction involves the oxidation of tyrosine to melanin intermediates DHI and DHICA, which then polymerizes into melanin [7, 8]. It has been observed that model systems for melanin are able to scavenge reactive oxygen species such as singlet oxygen ($^1O_2$), hydroxyl radicals ($^{\bullet}OH$) and the super oxide anion ($O_2^{-\bullet}$). This has lead to the belief that melanin may act as a free radical scavenger and antioxidant. This scavenging ability may be due to the numerous redox active moieties on the indole units assumed to be within melanin. These moieties may be oxidized as shown in (Fig. 2.3) [7].

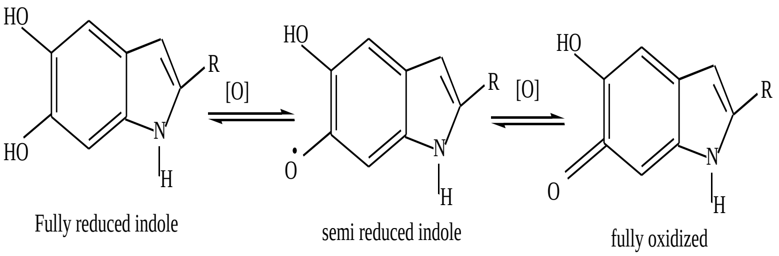


Figure 2.3: The oxidation of indole hydroxy groups to ketones [7].

Melanin has free radicals centres, which are exceptionally stable within the biomacromolecule. The formation of these radicals in melanogenesis, and also synthetic methods, is accompanied by hydrogen peroxide production. Furthermore, the formation of melanin consumes O_2. From these observations it has been suggested that melanin may form according to the following reaction mechanism [Eqn.1.1] [7].

$$\text{HO-}\Phi\text{-OH} + O_2 \longrightarrow \text{HO-}\Phi\text{-OH}^{\cdot} + O_2^{\cdot} + H^+$$

$$2O_2^{\cdot} + 2H^+ \longrightarrow H_2O_2 + O_2$$

Where HO-Φ-OH represents a fully reduced indole unit. The reduction of molecular oxygen (in its ground state) proceeds because of spin restriction in univalent free radical steps. These reactions form hydrogen peroxide, as required, and activate the indole units for the formation of melanin. Furthermore, the reaction showed in [Equ. 1.1] also demonstrates how the final redox active moieties within melanin may be oxidized as shown in (Fig. 2.3). It may also explain the chemical disorder of melanin since free radical mechanisms don't impose a great deal of control during reactions. The presence of free radicals in the final product is most likely due to indole units that have been activated but are unable to react, which is very much like the presence of free radicals in a classical polymer [7].

2.3 Biological functions

Even after the year of investigation, the role of melanin is not yet understood. Melanins absorbs strongly in the UV-visible region. Broad-band UV-visible absorbance characteristics allow melanins to function as Photoprotectants. Such a broad-band absorbance is very unusual for bimolecular and the actual mechanisms by which melanins absorb and dissipate energy are not yet understood. As a pigment, melanins are responsible for some of the colored patterns in the hair and skin of many vertebrates. This pigmentation can be of importance in both natural and sexual selection. In cuttlefish, Sepia officials, eumelanin is the pigment that colors the ink they release [3, 8].

2.3.1 The Important Role of Melanin as Protector against Free Radicals in Skin

The sun emits a wide spectrum of electromagnetic waves of which ultraviolet light (UV) is the most aggressive towards cellular compounds. UVR is the major environmental factor that influences the function and survival of many cell types and is regarded as the main causative factor in the induction of skin tumors. It has been traditionally believed that skin pigmentation is the most important photo protective factor. Large amounts of UVA and UVB are screened out by ozone, the major photo protective agent formed in earth's atmosphere. Hence, solar UV radiation that reaches the earth as well as our skin, is composed of 5-10% highly energetic UVB (290-315 nm) and 90-95 % UVA (315-400 nm) which is less energetic, but penetrates the skin deeper (Fig.2.4) due to its longer wavelength. Both UVA and UVB irradiation are very damaging to the skin. Depending on wavelength, UV damage occurs via different mechanisms. UVA mainly produces free radicals (FR)/reactive oxygen species (ROS) though interaction with endogenous photo sensitizers. These free radicals will cause indirect damage to DNA, proteins and membranes. Free radicals are believed to be involved in photo damage of dermal connective tissue cells and proteins. On the contrary, DNA with its aromatic, heterocyclic bases is a strongly absorbing chromophore for UVB (absorption maximum at 260- 265nm). Direct absorption of the UVB photons leads to disruption of DNA. So free radical reactions in the skin are one of the most interesting subjects of skin research because they are involved in various skin diseases, including skin tumors, skin wrinkling and skin aging. Following UV-exposure, free radicals play a major role in producing lipid radicals (L•) that seem to be responsible for the destruction of the cell membrane and ultimately the cell. Multiple lines of defense have evolved, aimed to protect skin from oxidative stress, including prevention, interception, and repair. The first defense line against UV generated free radicals in skin is caused by melanin contained in different qualities and concentrations in human skin characterizing different skin types. The existence of melanin in skin is strongly correlated with the prevention of free radicals generated by UV radiation. Especially in the skin (mainly eumelanin) ensures the only natural UV protection by eliminating the generated free radicals [9, 10].

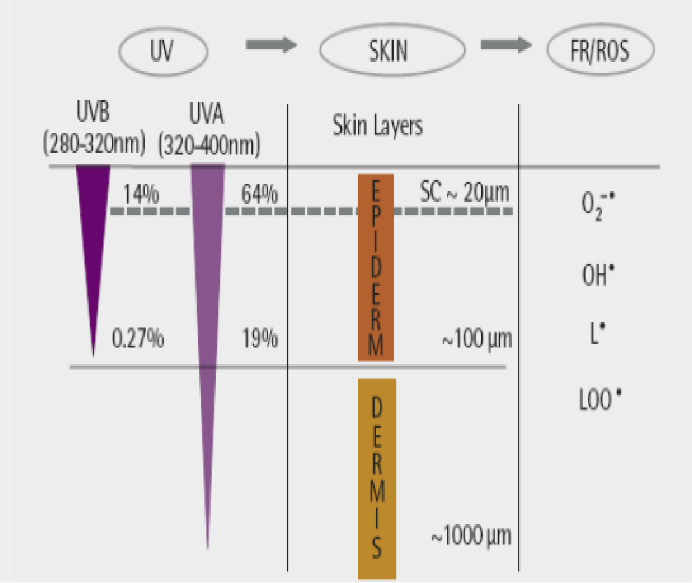


Fig. 2.4 Penetration of UVA and UVB radiation in the skin and the generated free radicals (FR) [9].

The free radical nature of melanin implies that it can act as free radical sink, protecting the body against free radical damage. This function of melanin also gives rise to hypothesis regarding its toxicity. Some researchers have shown that cells containing small amount of melanin are more susceptible to damage from irradiation. This observation has been linked to iron content of melanin, in that when melanin is saturated with transition metal ions like iron it may actually produce free radicals and therefore accelerates cell death rather than protecting it [3].

2.4. Melanin; The conductor

Since melanin is made of covalently liked dihydroxylindole (DHI) units, it fulfills the main requirements of a conducting polymer (conjugated polymer back bone). In this case, one may expect that melanin would behave similar to conducting polymers such as poly indole [3]. Indeed, McGinness *et al.* [7] found electrical resistance switching behavior within melanin, which is similar to that of amorphous inorganic semiconductors, suggesting that melanin can be thought of as an amorphous organic semiconductor. They and Baraldi *et al.* [7] found conductivities of 10^{-5} S cm^{-1} and 10^{-12} S cm^{-1} respectively, which is a difference of seven orders of magnitude. Both studies found that loss of water dramatically changed the electrical properties and the conductivities obtained are most likely due to differing water content in their respective samples. Baraldi *et al.* and Bridelli *et al.* [7] found evidence for two types of water in melanin: 'structural' water, probably within the structure of melanin; and 'physical' water, probably on the surface of melanin. They also found that water is a major factor in the electrical properties of melanin. Hall voltage measurements by Trukhan *et al.* [7] indicated that the charge carrier in melanin was positive. However, once again no hydration levels were recorded. It is most likely that the experiments were performed at ambient conditions; possibly indicating water's role in the result. They suggested that the charge carriers were holes but conceded that protons were also a likely interpretation [7]. Coulometric studies by Powell *et al.* [7] suggested that synthetic melanin carried charges that were 65% protonic and 35% electronic over a hydration range of 12% to 35% weight gained in water. Due to the thermoelectric measurements, they tried to explain the conductivity of melanin in terms of conformational changes in melanin's structure, which allows the electrons to hop more frequently. Further studies by Strzelecka investigated the supposed semiconductor properties of both natural and synthetic eumelanin. It was implied that the dominant charge carrier was a positively charged hole. In 1995, Jastrzebska *et al* [11] attempted to map out the direct current conductivity of melanin systematically as a function of hydration. They assumed that the hydration of melanin was proportional to relative humidity (RH). For this reason, they used various salt solutions to control the RH over a range of values. (Figure 2.5) shows the results obtained. They suggested that at low hydration the main charge carriers were electrons, but at higher hydration levels the carriers were positively charged polarons1 [7].

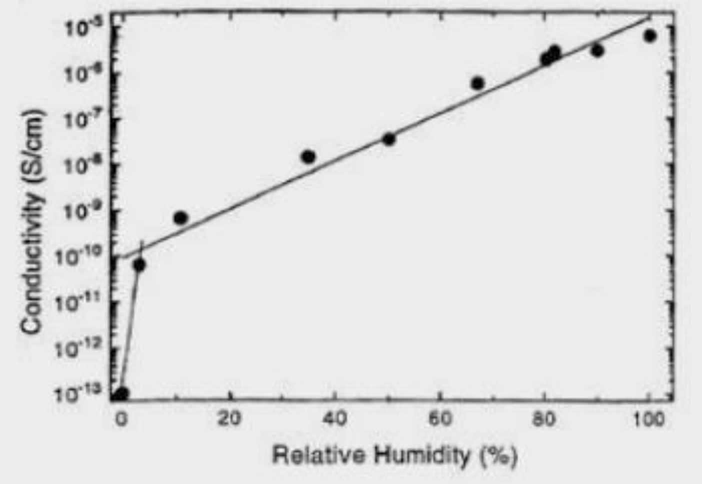


Figure 2.5: The conductivity of melanin as a function of RH at 298K, by Jastrzebska *et al.* Note that the y-axis is a log scale [7]

3. Electrochemical synthesis

3.1. Electrochemical Synthesis of conducting polymers

There are two main methods used in the synthesis of conducting polymers; chemical and electrochemical polymerization [3].

3.1.1 Chemical Polymerization

Chemical polymerization is the versatile technique for preparing large amounts of conducting polymers. Chemical synthesis can be carried out in a solution containing the monomer and an oxidant in an acidic medium. The common acids used are hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). Ammonium per sulfate ($(NH_4)_2S_2O_4$), potassium dichromate ($K_2Cr_2O_7$), cerium sulfate (Ce $(SO_4)_2$), sodium vanadate ($NaVO_3$), potassium ferricyanide (K_3 (Fe $(CN)_6$), potassium iodate (KIO_3), hydrogen peroxide (H_2O_2) and some lewis acids are typically used as oxidants. Oxidative chemical polymerizations result in the formation of the polymers in their doped and conducting state. Isolation of the neutral polymer is achieved by exposing the material to a strong reducing agent such as ammonia or hydrazine. An advantage of chemical oxidative polymerizations is that properly substituted heterocyclic and other aromatic monomers form soluble polymers. These polymers can be analyzed by traditional analytical techniques to determine their primary structure. The nature of the polymerization conditions also allows for easy scale-up and production of large quantities of polymer. Unfortunately, chemical oxidative polymerizations suffer from several disadvantages that often result in poor quality polymers. For example, Lewis acid catalyzed polymerizations yield the oxidized polymer, which is thought to be more rigid, resulting in its precipitation from the polymerization medium, limiting the degree of polymerization. Also, the use of strong oxidizing agents can result in the over oxidation and eventual decomposition of the polymer. Another disadvantage of this method is that the polymer results from solution containing an excess of oxidant and higher ionic strength of the medium. This leads to impurities of the materials that are certainly intractable [1, 2, 12].

3.1.2 Electrochemical Polymerization

Electrochemical synthesis of CPs involves the anodic oxidation of a monomer dissolved in a suitable electrolytic medium by applying an external potential, usually the monomer oxidation potential, to form reactive radical cations. The initial oxidation of monomer is followed by one of the two possible routes. The first route involves coupling of a monomer radical with a neutral monomer. A neutral dimer is formed after the second oxidation and loss of two protons. On the other hand, the second route involves the coupling of two radical cations followed by the loss of two protons to yield neutral dimmer. Then, the neutral dimer is oxidized and the process is repeated. Due to extended conjugation over two rings, the dimer has a lower oxidation potential than the monomer itself, and therefore it is oxidized easily to form the radical cation. As chain length increases, resulting oligomers become insoluble in the electrolytic medium and an electro active polymer film is deposited onto the working electrode. Because of the oxidative nature of electro polymerization, the deposited polymer is typically in its oxidized state and the positive charges along the polymer backbone are compensated by the supporting electrolyte anion. A proposed polymerization mechanism for heterocycles was given in (Fig. 3.1 (a)). During the polymerization, α-α couplings mainly afford a linear polymer backbone with electrical properties. On the other hand, the possible occurrence of α-β linkage causes the formation of branching and more defects in a given chain and therefore modifies its electronic distribution (Fig. 3.1 (b)). This is consistent with the considerable increase in the content of

disorder as well as the decrease in conductivity as the polymerization proceeds [2]
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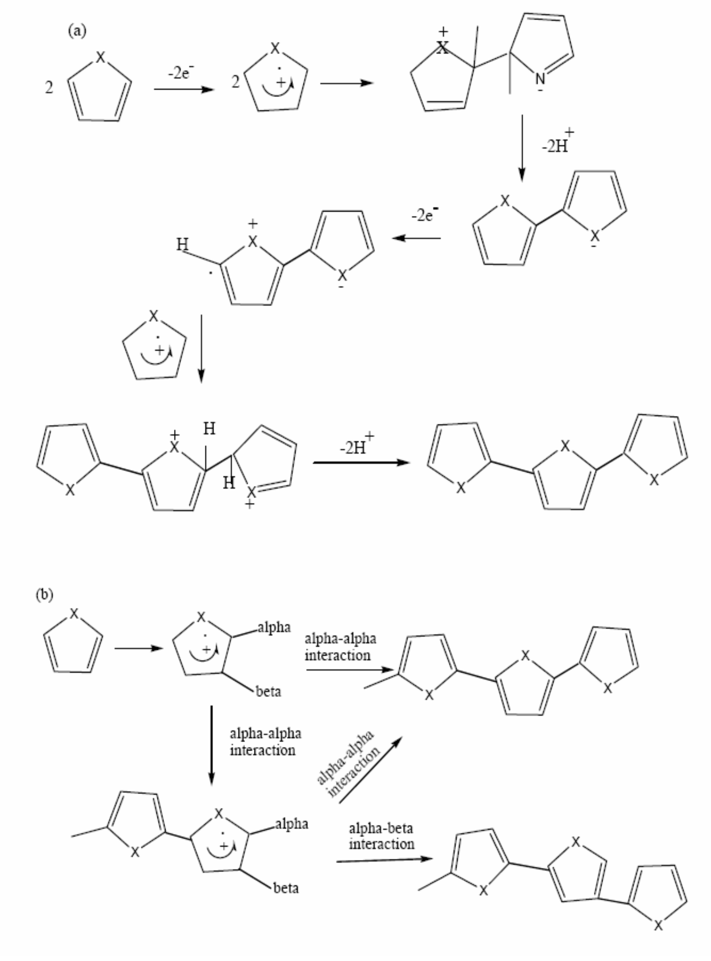

Figure.3.1.Electro polymerization mechanism. (a) Polymerization of heterocycles

(X = S, O, and NH), (b) Possible two linkage routes: a-a' and a-ß linkages in unsubstituted Poly (hetrocycles) [2]. Electrochemical polymerization of monomers on an electrode surface offers many advantages over chemical methods such as purity of the product and easy control of the thickness of the polymer films deposited on working electrodes. Similarly, the doping level can be controlled by varying the current and potential with time; synthesis and deposition of polymer can be realized simultaneously. In addition, the deposited films are easily amenable to numerous techniques of characterization such as UV-visible, infrared, and Raman spectroscopies. Therefore, this approach rapidly becomes the preferred method for preparing electrically conducting polymers [1].

3.2 Electrochemical Synthesis of melanin

Melanin can be synthesized through electro-polymerization of dl-dopa. [8] Although electrochemical analysis has been the main method used in the investigation of dopa it has not been widely thought of as a method of synthesis. The probability of electrochemical Synthesis of melanin has been hinted since 1974, when Brun et al. [3] investigated the electrochemical characteristics of dopa. However, they did not observe any deposit on the electrode. The first direct reference towards electrochemical polymerization of melanin was found in abstract by Z ielinski et al. in 1990. He claimed to have synthesized thin film of melanin electrochemically, but not followed by a full paper. Similarly the first paper published on the oxidative electrochemical Synthesis of melanin was presented by Horak et al. [3] in 1993, which oxidize DHI to form melanin on an electrode surface by means of cyclic voltammetry [3].

3.2.1 Dopant counter ions in melanin synthesis

Dopant counter ions are an important part of electrochemical Synthesis of CPs, since the choice of dopant greatly affects the mechanical and electrical properties of the polymer. Initially most conducting polymers were doped with simple inorganic salts such as iodide /chloride. However, the most common dopants used in the synthesis of conducting polymers such as polypyrrole are organic dopants containing sulphonated groups. In the synthesis of melanin the use of buffer implies the dopant counter ions are the inorganic buffer salts. Thus, the buffer used in the synthesis serves not only to maintain $_{P}$H, but also to the dopant counter ion. Another possible dopants used in melanin synthesis are metal ions since it has been shown that metal ions such as Cu^{2+}or Zn^{2+} affects the oxidation of melanin and may affect the ratio of DHICA to DHI in the polymer [3].

Conclusion

Nowadays, many different conducting polymers have been developed with wide range of properties and potential applications due to their chemical, mechanical, optical and electrical properties such as sensors, electromechanical devices, batteries and electrochromic cell. Melanins also serve as a free radical scavengers, antioxidants and photoconductors. However, some researchers have shown that cells containing small amount of melanin are more susceptible to damage from irradiation. This observation has been linked to iron content of melanin, in that when melanin is saturated with transition metal ions like iron it may actually produce free radicals and therefore accelerates cell death rather than protecting it. Therefore it is advisable to protect the melanin pigment from saturation with such transition metal ions. Electrochemical polymerization of conducting polymers from their monomers on an electrode surface offers many advantages over chemical methods such as purity of the product and easy control of the thickness of the polymer films deposited on working electrodes. Similarly, the doping level can be controlled by varying the current and potential with time; synthesis and deposition of polymer can be realized simultaneously. In addition, the deposited films are easily amenable to numerous techniques of characterization such as UV-visible, infrared, and Raman spectroscopies. Melanin can be synthesized through electro-polymerization of dl-dopa similar to any other conducting polymers. Therefore, this approach rapidly becomes the preferred method for preparing electrically conducting polymers.

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