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Review Paper

Electronics of Conjugated Polymers (I): Polyaniline

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Conducting polymers have elicited much interest among researchers because of their reasonably good conductivity, stability, ease of preparation, affordability and redox properties compared to other organic compounds. In particular, the electronic and electrochemical properties of conducting polymers have made them find applications in photovoltaic cells, organic light emitting diode and sensors. Among the conducting polymers, polyaniline has received much attention and intensive research work has been performed with the polymer in its native state or functionalized form. This is mainly due to the fact that polyaniline and its derivatives or composites or co-polymers with other materials are easy to synthesise chemically or electrochemically by oxidative polymerisation. The mechanism for the synthesis of polyaniline and its electronic properties are presented in this short review.

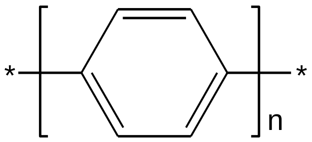
Keywords: Band gap, Conducting polymers, Polymerisation, Polyaniline, Semiconductors

1. INTRODUCTION

Traditionally polymers were seen as good electrical insulators and most of their applications had relied on their insulating properties[1]. However, until three decades ago researchers showed that certain class of polymers exhibits semiconducting properties[2]. Early studies showed that polypyrroles exhibit signs of conductivity[3]. This discovery was followed by the work of Shirakawa and co-workers in 1977 who reported the first synthesis of doped polyacetylene which was formed accidentally[4]. This incident took place when one of the co-workers mistakenly added excessive amount of catalyst in the reaction vessel for the polymerisation of acetylene .This resulted in the formation of a silver film instead of the expected black powder[4]. The new product had different optical properties compared to the normal black powder; hence by using iodine vapour they attempted to oxidize polyacetylene in order to obtain its normal optical properties. However, that only resulted in an increase in the conductivity of the polymer[4]. The discovery along with the extensive research in this area, contributed to authors (MacDiarmid, Heeger, and Shirakawa[5]) being awarded the Nobel Prize in Chemistry for the year 2000. Since this discovery reported by Shirakawa and co-workers, conducting polymers (CPs) have received much attention in the field of science. The aim of this review is to discuss the role of band gap and molecular orbital theories in determining the electronic characteristics of conducting polymers, with particular emphasis on polyaniline.

2. CONDUCTING POLYMERS

A conducting polymer is an organic based polymer that can act as a semiconductor or a conductor. The most widely studied organic polymers are polyaniline (PANI), polypyrroles, polythiophenes, and polyphenylene vinylenes[5-6] as given in Fig.1. They are conjugated, that is, they have π electron delocalisation along their polymer backbone, hence giving them unique optical and electrical properties [5-7]



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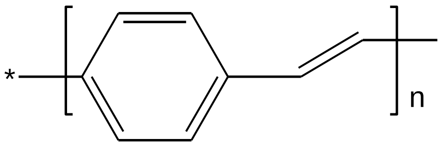
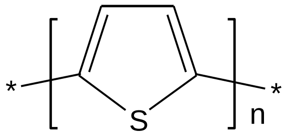


Polyphenylene vinylene



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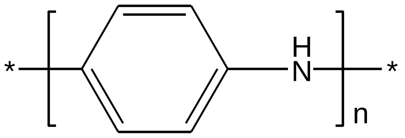
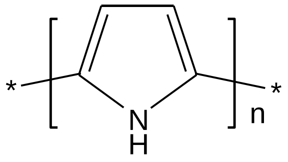
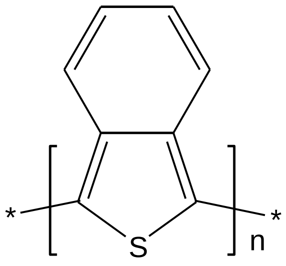


Polyaniline



Polypyrrole



Polyisothianaphthene

Figure 1. Typical (shown uncharged) structures of conducting polymers

2.1. Electronics of electrically conducting polymers (ECPs)

Conducting polymers are extensively conjugated molecules: they have alternating single and double bonds. In these molecules, electrons are able to move from one end of the polymer to the other through the extended p-orbital system[7]. Hence CPs are known to be either semiconductors or conductors, which are related to how bands and shells of electrons form within a compound. In view of the electronics of ECPs, the Band theory is employed to explain the mechanisms of conduction in CPs. The theory originates from the formation of energy bands in polymer materials from discrete orbital energy levels found in single atom systems. In this regard, it is vital to review band theory.

2.1.1. The band theory as a function of application of quantum theory

The physical chemistry approach to explanation of band theory is to relate it to the quantum theory of atomic structures. The first major success of quantum theory was its explanation of atomic spectra, particularly that of the simplest atom, hydrogen[8]. Quantum mechanics introduced an important concept which explained that atoms could only occupy well-defined energy states and for isolated atoms the energy states were very sharp [8]. The spectral emission lines which resulted correlated to electrons jumping from one allowed energy state to another, and this gave rise to correspondingly narrow line widths[8]. In a crystalline solid, atoms cannot be viewed as separate entities, because they are in close proximity with one another, and are chemically bonded to their nearest neighbour [9]. This leads to the concept that an electron on an atom sees the electric field due to electrons on other atoms and the nature of the chemical bond implies that electrons on close-neighbour atoms are able to exchange with one another, causing the broadening of sharp atomic energy states into energy ‘bands’ in the solid [9]. This can be illustrated using an example below in Fig 2, that depicts 3p and 3s electron shells for a single metallic atom in the third period of the periodic table that overlap to become bands that overlap in energy (Atkins, 2002)[9]. The association of these bands is no longer solely with single atoms but rather with crystal as a whole. In other words, electrons may appear with equal probability on atoms anywhere else in the crystal.

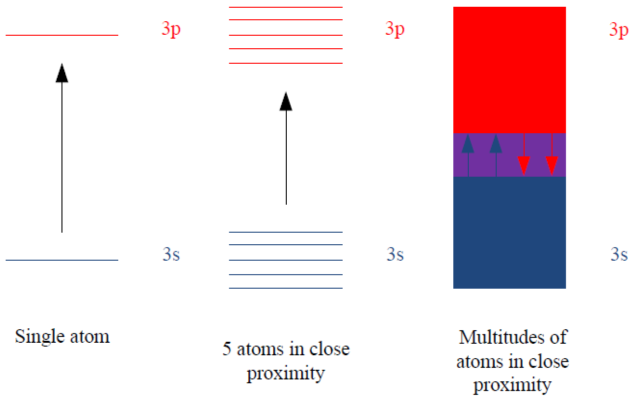


Figure 2. The formation of bands in a conducting solid in the 3rd period and overlap between the valence and conduction bands. Reprinted with permission from Reference [9].

2.1.2. The band theory as a function of application of molecular orbital theory

The chemical approach to band theory is to relate it to molecular orbital theory. In molecular orbital theory, using $H_{(1)}$ and $H_{(2)}$ hydrogen atoms as an example (Fig.3), an atomic molecular orbital from $H_{(1)}$ atom can overlap with an atomic molecular orbital of $H_{(2)}$. atom, resulting in the formation of two molecular orbitals known as the bonding and antibonding molecular orbitals[9]. These are delocalized over both atoms, and the bonding molecular orbital possess lower energy than the $H_{(1)}$ and $H_{(2)}$ atomic orbital, while the antibonding molecular orbital has higher energy.

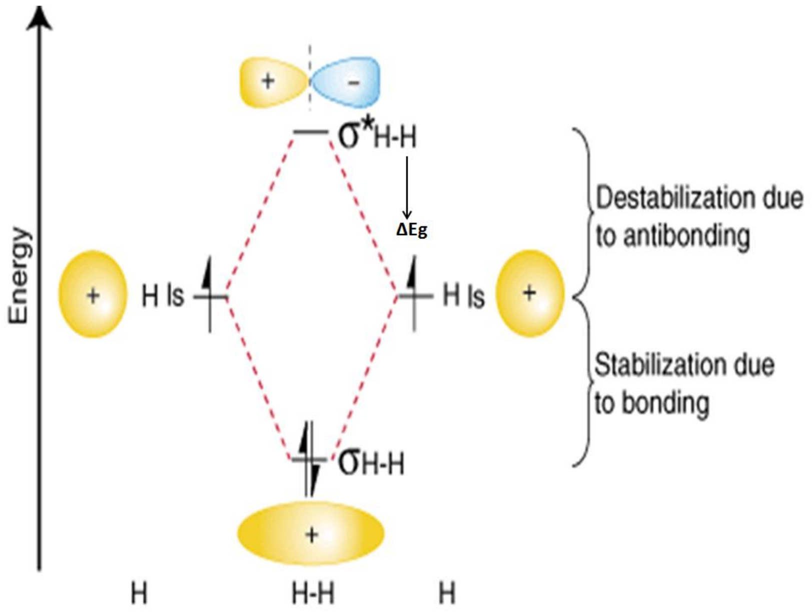


Figure 3. Molecular orbitals in a diatomic molecule.

The energy band that results from the bonding orbitals of a molecule is known as the valence band, while the conduction band is as a result of the antibonding orbitals of the molecule as illustrated in Fig. 4. The width of individual bands across the range of energy levels is called band width. The valence band (VB) represents the highest occupied molecular orbital (HOMO) and the conduction band (CB) represents the lowest unoccupied molecular orbital (LUMO**)**[10]. The gap between the highest filled energy level and lowest unfilled energy level is called band gap (E_g). This band gap represents a range of energies which is not available to electrons, and this gap is known variously as ‘the fundamental energy gap’, the ‘band gap’, the ‘energy gap’, or the ‘forbidden gap[8] The level of electrons in a system which is reached at absolute zero is called the Fermi level (F_g)[11]. It has been demonstrated that in order to allow the formation of delocalized electronic states, CPs molecular arrangement must be conjugated[2]. The delocalization of the electronic states relies on the resonance stabilized structure of the polymer. The size of the energy band gap depends on the extend of delocalization and the alternation of double and single bonds[10]. Moreover the size of the energy band gap will determine whether the CP is metal, semiconductor or insulator.[10] Combining the concepts explained in both atomic and molecular orbital theory, the electronic properties of metals, semiconductors, and insulators can be differentiated with reference to the energy band gap as shown in Fig. 4 below.

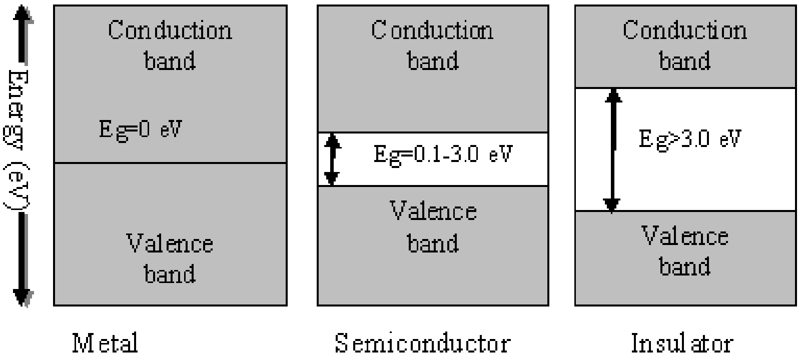


Figure 4. Energy band diagram demonstrating band gaps

2.1.3. The electronic properties of metals, semiconductors, and insulators

In metals there is no range of energies which is deemed unavailable to electrons, which simply means that forbidden gap or band gap in metals is $E_g = 0$ eV[12]. Hence metals always have a partially filled free-electron band, because the conduction and valence bands overlap. Hence the electron can readily occupy the conduction band[9]. Insulators have a band gap which is larger than 3 eV (Fig. 4)[12], the energy gap between VB and CB is too large, hence the electron is not able to make that jump to detach from its atom, in order to be promoted to the valance band. Consequently they are poor electrical conductors at ambient temperatures. Insulators can be defined as materials in which the valence bands are filled and the forbidden energy gap between valence band and conduction band is too great for the valence electrons to jump at normal temperatures from VB to the CB[9].

2.1.4. The electronic properties of semiconductors

There are two possible scenarios which can allow a material to become a conductor. The first instance is when the VB is not completely filled, hence an electron can raise its energy to a higher level within the valence band, so that it can detach from its atom[13]. This is coined as conduction within same band, and it requires a small amount of energy, hence many electrons are capable of accomplishing it. Second instance is when the band gap is very small, i.e. $E_g = 0.1 - 3$ eV, hence electrons can raise their energy and detach from their atoms by jumping to a higher energy level in the CB [13]. There are several methods, such as thermal or photochemical excitation, which can be used to excite electrons into the conduction band. Once these electrons have reached the conduction band, they contribute to the electrical conductivity[9]. Furthermore, the holes which are created in the valence band, by the electrons jumping to the conduction band, also contribute to electrical conductivity, i.e.

the transfer of charge (electrons or holes), through a polymers backbone causes conduction. Hence electrical properties of intrinsic semiconductors are determined by the number of electrons in conduction band and the number of holes in valence band[13]. However, another method known as doping is also used to generate the charge carriers (electrons and holes). As previously explained conjugation and the extent of delocalization in CPs determine the size of the energy band gap[10]. Generally the more conjugated the CP, the larger the energy band gap, hence most CP's are unstable in their undoped state[10]. Doping is a method that involves adding a different element into the material, and whether a semiconductor is pure (no different element added to it) or it is doped allows semiconductors to be categorized into either intrinsic or extrinsic semiconductors[12-13].

2.1.4.1. The electronic properties of intrinsic semiconductors

Undoped semiconductors such as pure silicon, is an example of an intrinsic semiconductor. It possesses a relatively small forbidden energy gap (E_g). Hence because its E_g is small, at 300 K (i.e. room temperature) the electrons can be thermally excited, causing them to be raised to higher energy in the conduction band, yielding about 10^{15}-10^{20} conduction electrons[10]. Fig. 5 demonstrates the concept of intrinsic semiconductors. As the temperature is increased, more electrons are thermally excited to the conductions bands and leaving more holes in the valence band.

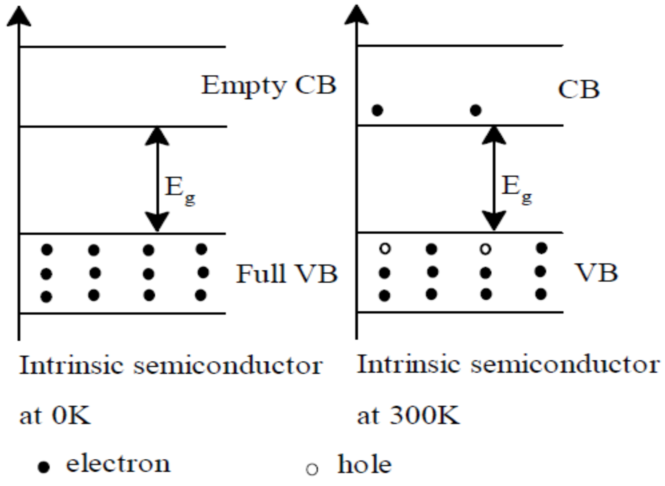


Figure 5. Band structure diagram of an intrinsic semiconductor[12] (Reprinted with permission)

2.1.4.2. The electronic properties of extrinsic semiconductors

Semiconductor materials into which another element or an impurity is introduced are known as extrinsic semiconductors. The impurity is known as the dopant, and the process of adding it is referred to as doping. Dopants are categorised into two groups, i.e. they can either be donors or acceptor[10]. Examples of elements which are donors are phosphorus, arsenic and antimony and typical acceptor elements in extrinsic semiconductors are trivalent elements such as boron, indium, gallium and aluminium[12]. Furthermore, in an extrinsic semiconductor there are two types of conduction mechanisms. The first mechanism is when an acceptor element is doped with a donor element that has a higher valence number than it [9]. For example, germanium atom has 32 electrons distributed in four orbits. The outermost orbital is called the valence orbital, and it contains four electrons, hence it is tetravalent. If Ge is doped with phosphorous, which has a valence orbital which contains five electrons (pentavelent), this creates an extra electron per atom[12]. This extra pair of electrons from donor phosphorus partially fills the conduction band because it occupies discrete levels near the bottom of the conduction band, around -0.1 eV of the band gap[12] At room temperature (300 K) the electrons are excited into the conduction band. This type of conduction is called n-type semiconductivity and uses electrons as the main charge carriers [10] as illustrated in Fig.6 below.

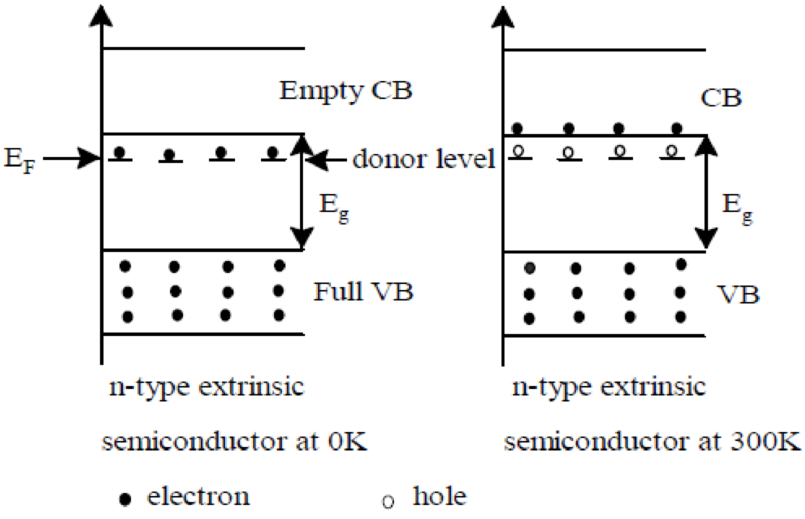


Figure 6. Band structure diagram of an extrinsic n-type semiconductor

In the second mechanism, a dopant with a lower valency than the material that is being doped is used, for example a trivalent dopant, such as indium, can be used to dope germanium. In this scenario, only three covalent bonds are formed from the four possible bonds which could form. Here, the valence band is now depleted of some electrons because the fourth possible bond is vacant. This vacancy creates a hole for each electron missing from a bonding pair[12]. The main charge carriers in this instance are the holes that are formed when the electrons move out of the valence shell. A trivalent dopant is characterized as an acceptor because it injects many holes which are the majority carriers of the charge. These holes are responsible for the conductivity of crystals. For this reason the materials are called p-type semiconductors[9-10, 12-13]

The electronic properties of CPs and the general band theory described above provide the insight that can direct the process of designing and synthesising conducting polymers in order to achieve the desired electronic properties. Polyaniline, polypyrroles, polythiophenes and polyphenylene vinylenes[6-7] are among the most widely studied materials in the family of conducting polymers. However, PANI is probably the most important industrial conducting polymer[6] due to the fact that it can be processed from solutions into thin film[14], exhibits high environmental stability, has low synthetic cost[15] and the fact that its morphological, electric and optical properties can be controlled by doping and deprotonation[16]. These unique properties of PANI necessitated its applications in areas such as energy storage (light weight batteries, capacitors)[17], energy conversion (photovoltaic cells), optical signal processing (light emitting diodes)[2, 17-18] and electrocatlysis.

2.2. Polyaniline

Polyaniline was initially discovered in 1834 by Runge, and it was referred to as aniline black[19]. Following this, Letheby carried out research to analyse this material in 1862 [19]. PANI is known as a mixed oxidation state polymer composed of reduced benzoid units and oxidized quinoid units[15]. Green and Woodhead (1912)[20] discovered this interesting characteristic of polyaniline. Furthermore, it was discovered that PANI had characteristics of switching between a conductor and an insulator under certain experimental conditions[1]. Since then, the material has become a subject of great interest in research[21].

2.2.1. Structure of Polyaniline

As a mixed oxidation state polymer consisting of benzoid and oxidized quinoid units[15, 22], PANI's average oxidation state is denoted as 1-y whereby the value of y determines the existence of each of the three distinct PANI oxidation states[15, 20] as shown in Fig. 7. Thus PANI exists as fully reduced leucoemeraldine (LE) where 1-y = 0, half oxidized emeraldine base (EB) where 1-y = 0.5 and fully oxidized pernigraniline (PE) where 1-y = 1[15]. The EB is regarded as the most useful form of polyaniline due to its high stability at room temperature, it is composed of two benzoid units and one quinoid unit that alternate and it is known to be a semiconductor[23].

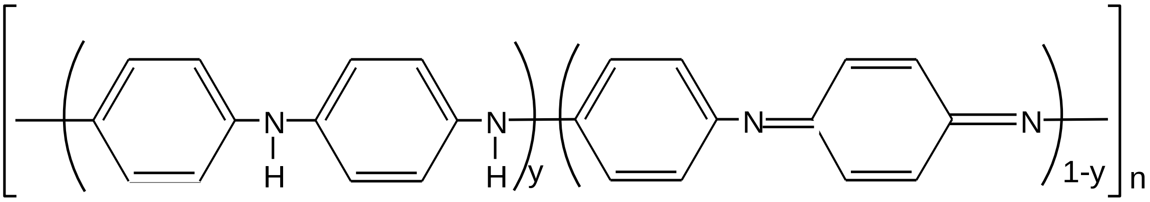


Figure 7. Different oxidation states of polyaniline (y = 1: leucoemeraldine, y = 0.5: emeraldine and y = 0: pernigraniline

Furthermore, EB can be doped in a non-redox reaction in acidic medium which results in an emaraldine salt (ES). On the other hand LE is easily oxidized while the PE is easily degraded[15, 23].

2.2.2. Synthesis of polyaniline

There are several methods that can be employed to synthesize conducting polymers; such as electrochemical oxidation of the monomers and chemical synthesis[24]. Moreover uncommon methods such as enzyme-catalyzed polymerisation and photochemically-initiated polymerisation are also employed[25] in some instances. Essentially during polymerisation, monomers are used as starting materials to form low molecular weight oligomers. At potentials that are lower than that at which the monomers are oxidized, the low molecular weight oligomers are further oxidized to form a polymer[24]. In the case of electrochemical polymerisation, the monomers have to be oxidized by cycling between a potential window which will allow for the oxidation to take place and the polymer will then be electrodeposited onto the substrate[24-25]. In the case of chemical synthesis chemical oxidants such as ferric chloride ($FeCl_3$) and ammonium persulfate [$(NH_4)_2S_2O_8$] are employed and the polymer precipitates out of the chemical reaction solution[24]. The current review focuses on electrochemical and chemical polymerisation and these will be further discussed.

2.2.3. Electrochemical polymerisation

Electrochemical polymerisation is commonly carried out by employing one of three techniques. These methods involve the application of (i) a constant voltage (potentiostatic), (ii) a variable current and voltage (potentiodynamic) and (iii) a constant current (galvanostatic) to an aqueous solution of aniline[26]. To carry out electropolymerisation by using any of the three mentioned techniques, a three electrode assembly is required. These electrodes are known as counter electrode, reference electrode e.g. Ag/Ag chloride and a working electrode. There electrosynthesized polymer is deposited onto the working electrode which can be a platinum gold, glassy carbon or indium tin oxide (ITO). An electrolyte such as an acid (HA) is also needed for polymerisation[27]. It has several functions such as, to provide a sufficiently low pH so as to help solubilize the aniline monomer in water and to avoid excessive branching of undesired products, but instead to generate doped emeraldine salt (ES) form [27].

2.2.4. Chemical polymerisation

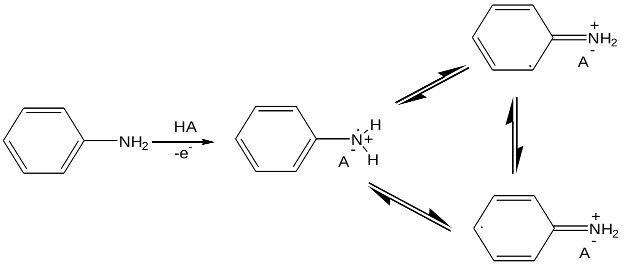
For chemical polymerisation to take place monomers have to be oxidized to initiate the reaction. $(NH_4)_2S_2O_8$ which has oxidation potential ($E_0 = 1.94$ V) and $FeCl_3$ with $E_0 = 0.77$ V are the most commonly used oxidizing agent[28]. However, there are other less commonly used oxidants such as hydrogen peroxide [(H_2O_2); $E_0 = 1.78$ V], cerium (IV) sulfate [$Ce(SO_4)_2$; $E_0 = 1.72$ V] and potassium dichromate [$K_2Cr_2O_7$; $E_0 = 1.23$V][26]. Ferric chloride has the lowest oxidation potential compared to the other four oxidizing agents but it has proved to be a useful oxidizing agent yielding up to 200000 molecular weight polyaniline chain[20]. As is the case with electrochemical polymerisation, acidic pH conditions ($pH < 3$) are required for a chemical polymerisation. The low acidic pH minimises the formation of undesired branched product[29] .

2.2.5. Mechanism of polymerisation

The chemical or electrochemical polymerisation of aniline proceeds via a radical propagation mechanism as shown in Schemes 1-6. The initial steps (1 and 2) are common to both methods, but subtle differences appear in the initial product of the chain propagation step and product formation steps (3 and 4)[30]. Accordingly steps 3 and 4 will be illustrated separately for chemical and electrochemical polymerisation[25].

Step 1: Oxidation of Monomer

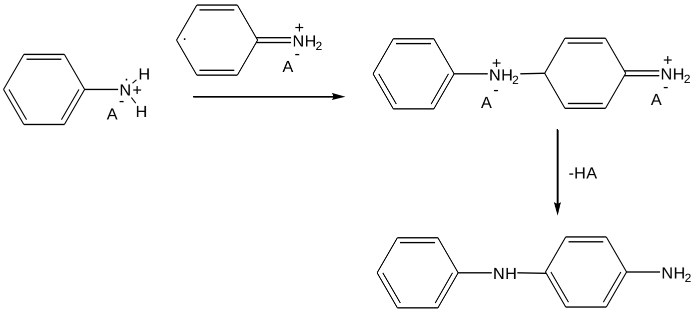
In the initial step, as shown in Scheme 1, the oxidation of aniline to a radical cation, which exists in three resonance forms, takes place. This step is the slowest step in the reaction, hence it's deemed as the rate determining step[30] in aniline polymerisation.



Scheme 1. Oxidation of monomer during electrochemical polymerisation of aniline.

Step 2: Radical coupling and re-aromatisation

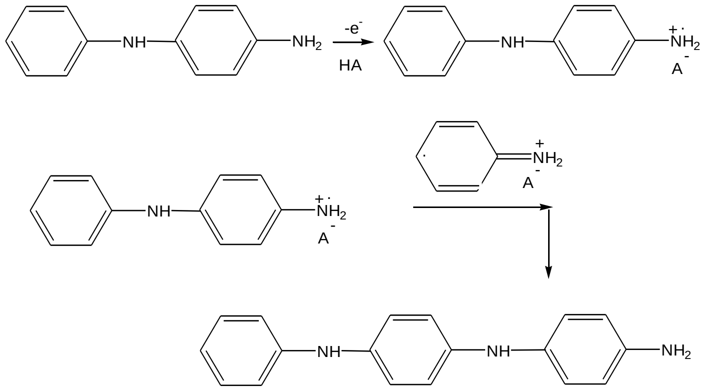
Head to tail coupling of the *N*- and *para*- radical cations (Scheme 2) takes place, yielding a dicationic dimer species[31]. This dimer further undergoes the process of re-aromatisation which causes it to revert to its neutral state, yielding an intermediate referred to as *p*-aminodiphenylamine (PADPA). These processes are also accompanied by the elimination of two protons[30].



Scheme 2. Radical coupling and re-aromatization during electrochemical polymerisation of aniline[30].

Step 3 : Chain propagation for electrochemical synthesis

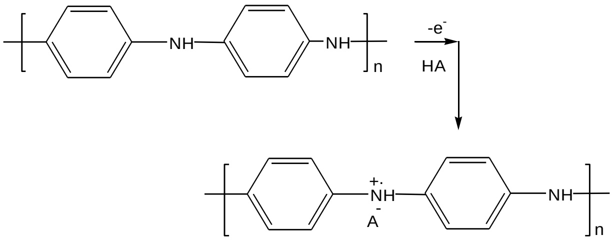
The dimer radical cation (centred on the para position; nitrogen atom) undergoes oxidation on the surface of the electrode[30]. Chain propagation results from the radical cation of the dimer coupling with an aniline cation as illustrated in Scheme 3.



Scheme 3. Chain propagation during electrochemical polymerisation of aniline.

Step 4 : Oxidation and doping of the polymer for electrochemical synthesis

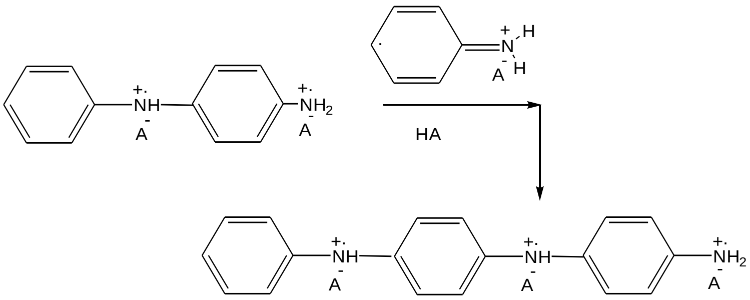
Scheme 4 shows the oxidation and doping of the polymer during electrochemical polymerisation reaction in acid solution which dopes the polymer to yield PANI/HA[31].



Scheme 4. Oxidation and doping of the polymer during electrochemical polymerisation of aniline.

Step 3 : Chain propagation for chemical synthesis

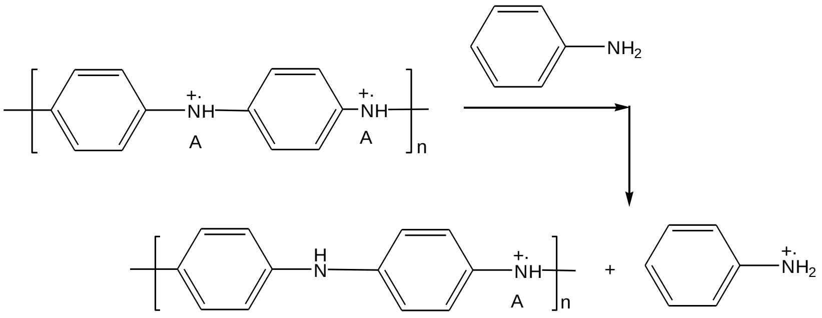
In the chain propagation during the chemical synthesis of polyaniline, the initial product is the fully oxidized pernigraniline salt as shown in Scheme 5 below.



Scheme 5. Chain propagation of the polymer during chemical polymerisation of aniline.

Step 4: Reduction of the pernigraniline salt to emeraldine salt

When all the oxidant in the reaction mixture is completely used up, the pernigraniline salt formed in step 3 of the chemical synthesis mechanism is reduced by unreacted aniline to the green emeraldine salt (Scheme 6).



Scheme 6. Reduction of the pernigraniline salt to emeraldine salt during chemical polymerisation of aniline[26].

2.2.6. Properties of polyaniline

It is well known that polyaniline has switching, optical, conductive and solubility properties that distinguish it from other conducting polymers (Wallace *et al*., 2002) [22]. These properties of aniline will be discussed in this section.

2.2.6.1. Switching and Optical properties of PANI

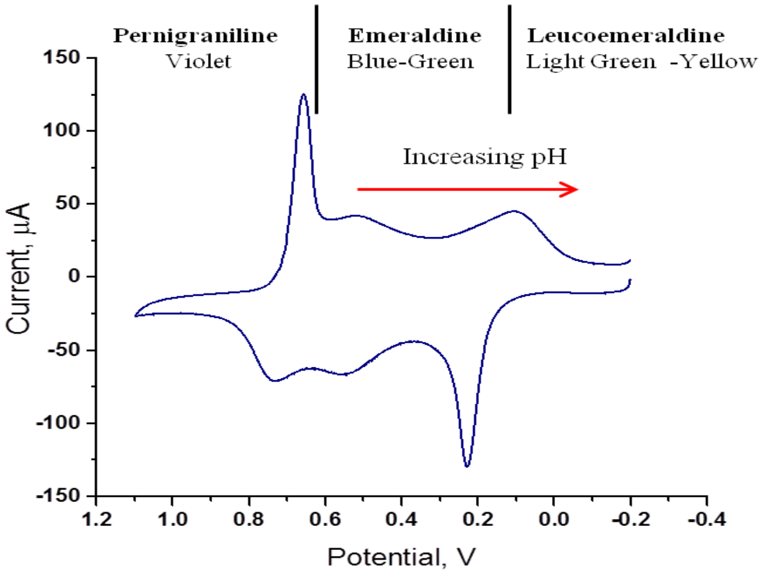


Figure 8. Cyclic voltammogram of polyaniline film on a platinum electrode in 1 M HCl at a scan rate 0.1 V s^{-1}. (The potentials at which structure and colour changes occur and the change in the potential of the second redox reaction with pH are shown as well).

The switching and optical properties of PANI are interlinked and influence each other directly. The tendency of PANI to switch between oxidation states directly influences it's UV-vis absorption characteristics[26], and as a result the two properties will be discussed concurrently. Once the conductive form of the PANI is formed, i.e. emaraldine salt, the addition of an acid or a base that protonates and deprotonates the base (-NH-) sites in PANI causes switching of PANI between oxidation states [32].

This means that there is a pH dependence of the oxidation states of PANI. When the pH of the polymerisation reaction is greater than four PANI becomes non-electroactive. The loss of its electroactivity is due to the failure of the formation of the ES salt [32]. PANI is a mixed oxidation state polymer, ranging from the most reduced leucoemerladine form which is yellow in colour, to the half oxidized emerladine which is green, and the violet fully oxidized pernigraniline[33] as illustrated in Fig. 8. The electrochemical switching of polyaniline between oxidation states can be readily monitored by cyclic voltammetry as illustrated in Fig. 8. The voltammogram shows the trend of structural switching of PANI with pH and redox potentials. Furthermore the UV-visible spectrum of polyaniline is sensitive to oxidation state and transitions between oxidation states and is accompanied by visible optical colour change [32]. Hence, absorbance parameters of the polymer can be used to calculate the electronic band gap of the various PANI structures. The absorbance characteristics are also linked to the signature transitions which take place during the switching between oxidation states of PANI. When quantifying the band gap of the different oxidation states with UV-visible data, the electronic band structures are linked to one of the oxidation states of PANI[34]. The PANI in the ES form exhibits three characteristic bands, one at 330 nm attributed to π-π* band, and two bands at 430 and 800 nm in visible region which are due to π-polaron band and polaron-π* band transitions[35] as illustrated in Fig. 9.

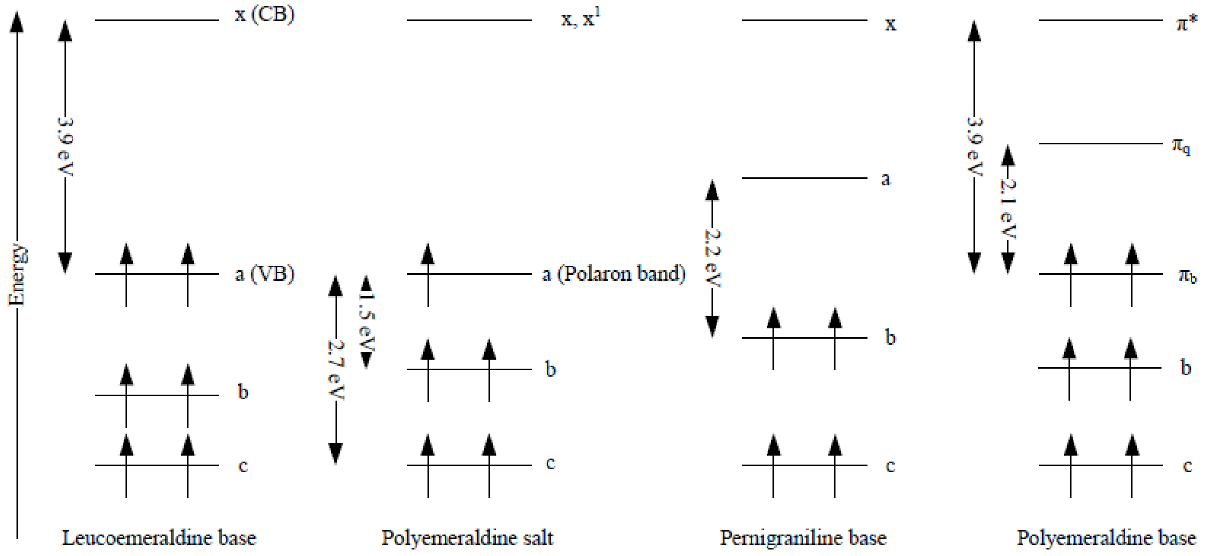
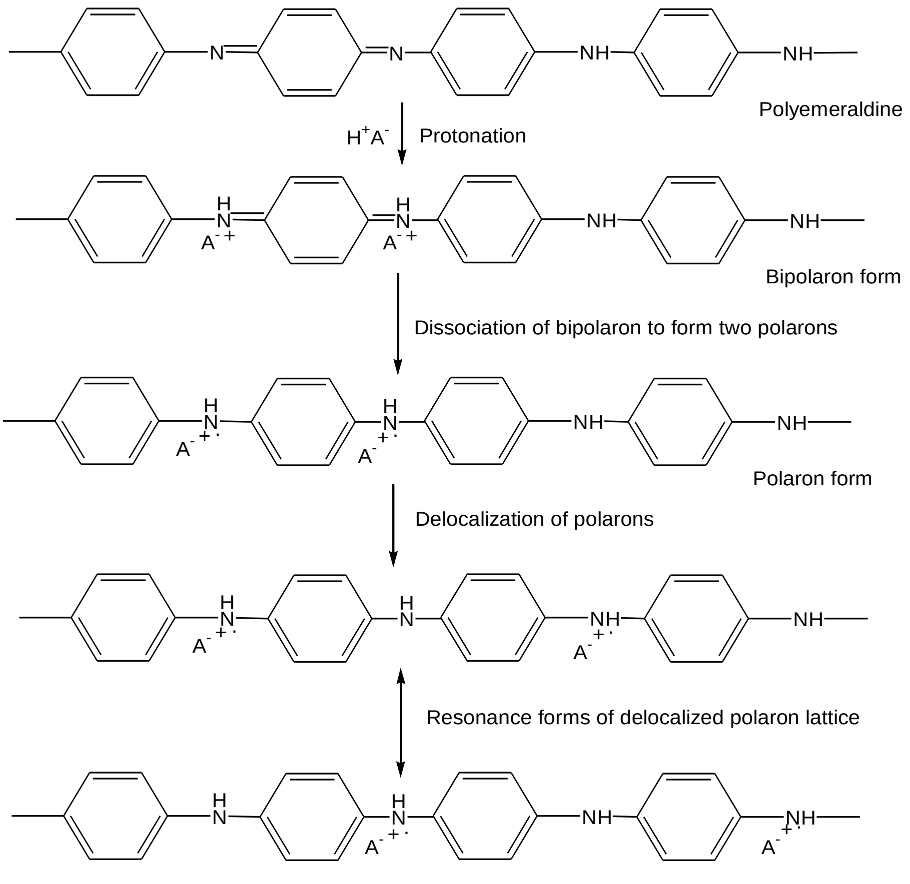


Figure 9. The different band gaps present in polyaniline redox states[34]. (Reprinted with permission)

The emeraldine base form of PANI shows a low wavelength π-π* band and a strong absorption band at ca. 600 nm attributed to a local charge transfer between a quinoid ring and the adjacent imine-phenyl-amine units (intramolecular charge transfer exciton)[25]. The reduced leucoemeraldine base exhibits a band at ca. 320 nm attributed to the π-π* electronic transition[34]. Pernigraniline base shows two bands at ca. 320 nm (π-π* band) and at ca. 530 nm (Peierl gap transition)[25].

2.2.6.2. Conductivity properties of PANI

It has been previously demonstrated that the polyaniline chain can be formed by various combinations of the two repeating units known as the X and Y components of polyaniline[34]. Owing to this, PANI has many unique properties and electronic conduction mechanisms that distinguish it from the rest of the conducting polymers. For example the conductivity of PANI varies with the extent of oxidation (variation in the number of electrons) and the degree of protonation (variation in the number of protons).



Scheme 7. The doping of EB with protons to form the conducting emeraldine salt (PANI/HA) form of polyaniline (a polaron lattice)[26] (Reprinted with permission)

Among the various oxidation states that PANI can exist in, the one that can be doped to a highly conductive state is the moderately oxidized emeraldine base[32]. This form of PANI has a structure which consists of equal proportions of amines (–NH–) and imine (=N–) sites. Through protonic acid doping, imine sites are protonated by acids HA to the bipolaron (dication salt) form[36]. The bipolaron then undergoes a further rearrangement to form the delocalized polaron lattice which is a polysemiquinone radical-cation salt as shown in Scheme 7 below. The resulting emeraldine salt has conductivity on a semiconductor level of the order of 100 S cm^{-1}, which is many orders of magnitude higher than that of common polymers ($<10^{-9}$ S cm^{-1}) but lower than that of typical metals ($>10^{4}$ S cm^{-1})[37]. Only 1% of the charge carriers which are available in the ES salt actually contribute to its observed conductivity. If all the available charge carriers were to contribute, the resulting conductivity at room temperature would be ~ 10^{5} S cm^{-1}, which is comparable to that of copper[38].

2.2.6.3. Solubility properties of PANI

The emeraldine base, which is a less ionic state of PANI, is soluble in a number of organic solvents such as, dimethyl sulfoxide, chloroform, tetrahydrofuran, dimethyl formamide, and methyl pyrrolidinone[39]. This is because in this state there are no cationic charges present in the polymer backbone. However, the emeraldine salt is insoluble in aqueous solutions and most common organic solvents because in this state PANI has cationic charges present in its polymer backbone[39]. It has been demonstrated that by introducing functionalised protonic acid dopants such as sulfonic acids (10-champhor sulfonic acid and dodecyl-benzene sulfonic acid) into the ES salt, solubility can be improved although it will be limited[40]. Furthermore, poly(2-methoxyaniline-5-sulfonic acid) (PMAS) has been reported to give a unique nanoscale water-soluble material containing a conducting PANI backbone and a conducting PMAS dopant, which exhibits multiple switching capabilities[41]. Another example of a sulfonated PANI derivative is polyanilino naphthathelene sulfonic acid (PANSA) which is synthesized from 8-anilino1-naphthalene sulfonic acid monomer. The monomer is viewed as aniline substituted with naphthalene sulfonic acid. It has been reported in an experiment where PANSA was used as a platform for preparing an enzyme-based biosensor for the determination of ethambutol[42], that the presence of naphthalene sulfonic acid aids the solubility of the polymer.

3. CONCLUSION

The propensity of the morphology of polyaniline to be customised by controlling the synthesis conditions has resulted in the production of polyaniline of various structural descriptions including nano-tubes, nano-rods and nanoparticles. This structural changes that are realisable with polyaniline are made possible by the use of dopants such has high molecular weight sulfonic acids. Accordingly, the variations in the molecular aggregation of the polymer mean that a range of band gaps, electronic and electrical properties are realisable with doped polyaniline. This, therefore, makes it possible for the polymer to have a wide application in electrochemistry, sensors and electrochemical energy systems.

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