Polyaniline: Synthesis Methods, Doping and Conduction Mechanism

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Abstract

Among all the conducting polymers, polyaniline holds a special position, due to its unique properties such as low cost of monomers (aniline), distinguishable electrical properties, excellent redox reversibility, high environmental stability and can be easily polymerized in labs either by chemical or electrochemical methods. The electrical properties of polyaniline pretty much depend upon the doping agents, protonation of the constituent units in the chain backbone, and water content. Conductive nature of polyaniline makes it a versatile conducting polymer for variety of applications such as gas sensors, supercapacitors, lithium ion batteries and photovoltaic cells. The objective of this chapter is to provide basic concept of polyaniline synthesis and its doping mechanism. We hope that this chapter will be useful for academic as well as for research on polyaniline.

Keywords: polyaniline, synthesis, doping, dedoping, conduction mechanism

1. Introduction

The polymers to which we are more familiar are plastics—that do not conduct electricity, it means they behave as insulators. The commercial plastics which are made up of saturated organic polymers are insulators, in contrast those plastics are made up of conjugated polymers have the property of semiconductors. Scientists Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have changed this concept with their pioneer invention—that a polymer can behave as electricity conductor almost like a 'metal'. Indeed, the polymers that have conjugation in their repeating units combine the electrical properties like traditional inorganic materials while providing mechanical flexibility and low cost. In 1974 Shirakawa and his coworkers synthesized free standing polyacetylene film with silvery appearance using Ziegler-Natta catalyst, but it was electrically insulator. Somewhat later in 1977, Shirakawa, together with MacDiarmid and Heeger discovered that the polyacetylene can be made conductive after exposing it to the oxidizing agents like chlorine, bromine or iodine which made polyacetylene 10^9 times more conductive than the pristine polyacetylene [1]. For which they were awarded Nobel Prize in 2000. This breakthrough gave the rise to the development of new kind of materials with combine the properties of plastic and electrical conductivity.
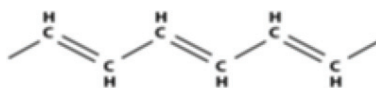
Polyacetylene

> *"Unlike plastic, conducting polymers have alternating single and double bond with sp^2 hybridized structure in conjugated sequence along the chain backbone of the polymer, which acquires delocalization of π-electron and consequently leads electrical conduction".*

Since the discovery of conductive polyacetylene, the interest in conducting polymers has emerged through in three stages: (a) the preliminary interest driven by their unique properties and practical possibilities; (b) owing to the complications in processing and poor mechanical properties; and (c) following the discovery of solution and melt processability [2–4]. Though, a variety of conducting polymers have been synthesized and investigated, polyaniline (PANI) is one of a class of organic polymers that are intrinsically conducting. PANI and its derivatives are being studied massively owing to their good combination of properties such as stability, low price, ease of synthesis, and interesting redox properties associated with its constituent's units along the chain backbone of the polymer. Between each repeating benzenoid and quinoid moieties there is nitrogen in the form of imino and amino groups, which can be protonated and deprotonated. The conduction of charge in conducting polymers has been of prime focus since the synthesis of polyacetylene. The electrical conduction in polymer chain segments is depends upon the several factors such as (a) method of synthesis, (b) method of processing of polymer, (c) degree of crystallinity of polymer and (d) temperature. The unique combination of properties of conducting polymers have led to considerable fundamental and technological interest in conducting polymers based materials over the few decades, especially in organic electronics. However, the potential technological applications of conducting polymers often require reasonable good conductive materials. The electrical conductivity properties of the conducting polymers depend upon the doping counter ions. Unlike other conjugated polymers, the electrical conductivity of PANI is affected by doping and protonation of the polymer segments. Doping is a reversible to produce original polymer with little or no damage of polymer backbone. In doped state, the polymer chain backbone consists of a delocalized π-system. In undoped state the polymer chain backbone may have conjugation like in polyacetylene but without conductivity, however, in case of PANI (leucoemeraldine base form) gains conjugation only after doping or non-conjugated form of PANI that is emeraldine base becomes conjugated only after protonic acid doping. Conducting polymers containing π-conjugation system may be doped without changing the number of electrons associated with polymer chain backbone. However, the energy level is rather rearranged during doping process. Therefore, the way to dope the polymer without involving redox chemistry is the protonic acid doping. The acid doping level can be tuned by simply controlling the pH of dopant solution. Among the conducting polymers PANI is the primary example of doping to make highly conductive material. The emeraldine base form of PANI is somewhat like an alternating block copolymer, during doping by acid dopant emeraldine base converts into emeraldine salt form. The proton induced spin unpaired mechanism leads to a structural change with one pair unpaired spin per repeat unit without any alter in the number of the electrons. This remarkable interconversion in PANI forms leads non-conductive behavior to highly conductive

behavior. This phenomenon has very well described in the literature but it is still not very well understood from the point of basic theory. Under this chapter we shall shed some light upon doing and conduction mechanism of PANI with taking the help of earlier reported research.

2. Synthesis of PANI

PANI can be synthesized by chemical or electrochemical method both methods have own advantages. For example, through chemical process PANI can be synthesized in powder form and in bulk amount, this is often difficult with electrochemical process. However, by electrochemical technique PANI can be deposited on various conductive substrates in the form of thin films, especially for the use in electronic devices. In chemical synthesis, typically, aniline monomers are oxidized by oxidizing agents such as ammonium persulfate, hydrogen peroxide, ferric chloride, and ceric nitrate/sulfate) in acidic medium (hydrochloric acid and sulfuric acid) [5–8]. Generally, the chemical synthesis of PANI involves the use of acid medium containing oxidizing agent and aniline monomers in water solution. During reaction, the function of oxidizing agent is to remove a proton from aniline unit without forming coordination complex, then the polymerization of aniline monomers proceeds through redox process conjoining repeating monomer units [9]. Which is most favorable for the production of PANI product in bulk amount. In presence of oxidant (oxidizing agent) the polymer product undergoes oxidation at a lower potential than the constituent reactant (aniline monomer) in acidic environment (below 3–4 pH). It is also interesting to note that the high molecular weight PANI can be obtained during the polymerization by lowering the temperature of the reaction near to ~0°C. In general, for chemical synthesis procedures an aqueous electrolyte medium is required to polymerize aniline monomers. Recently, Khalid et al. [10] has developed a novel water-free synthesis of PANI, in which organic phase-tetrahydrofuran was used instead of water, unlike traditional chemical method. The oxidative polymerization of aniline in presence of aqueous acid solution has been shown below (**Figure 1**).

The first electrochemical synthesis of PANI was proposed by Letheby in 1962 [11] when he observed the growth of a blue-green powder pigment on platinum anode electrolysis of a solution of aniline and sulfuric acid. The adherent thin films of PANI can be electrodeposited through potentiostatic process by applying constant potential between the range from 0.5 to 0.9 V with several seconds to minutes, which involves placing three electrodes (working, counter and reference) into the solution containing monomers and electrolyte (HCl, and H_2SO_4) [12]. Galvanostatic and potentiodynamic methods can also be used for the electrodeposition of PANI. For electrodeposition, the three-electrode cell system is employed using Pt counter, silver-silver chloride reference, and ITO or (Cu, Fe, Au, graphite) working electrodes. The main advantage of electrochemically prepared PANI is to obtain clean and ordered thin film in desirable shape and size. In
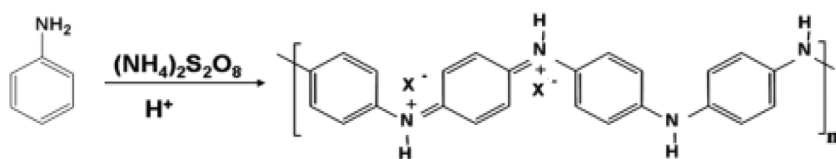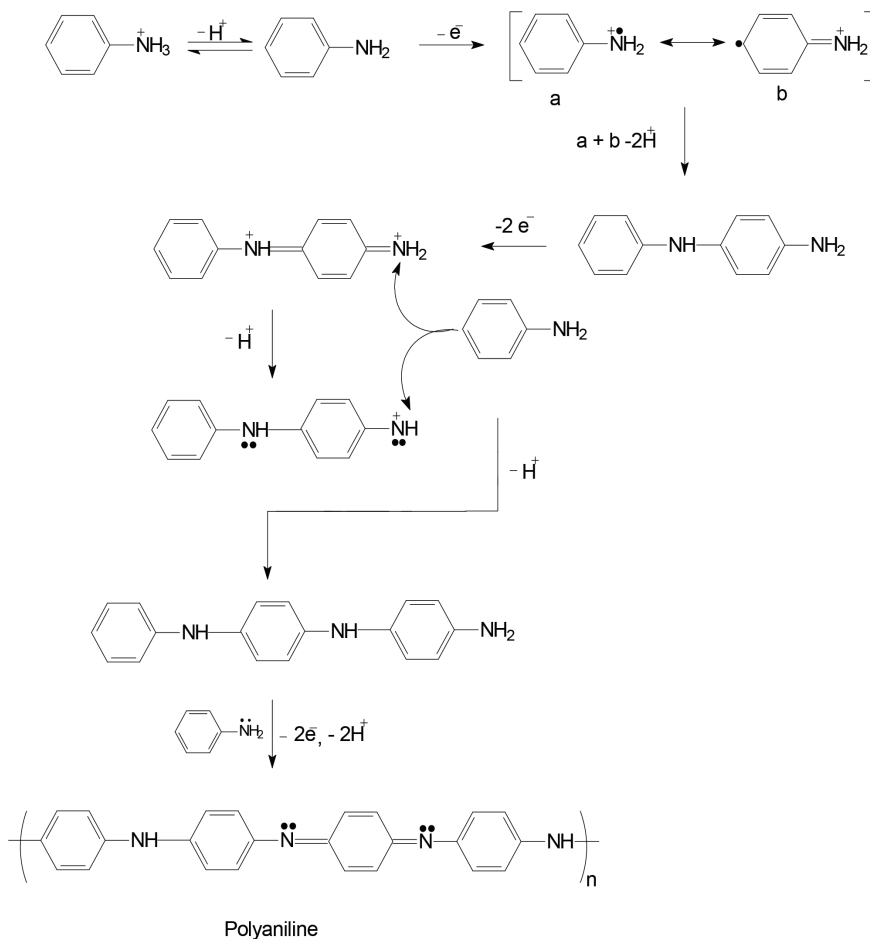

Figure 1.
Oxidative polymerization of aniline to polyaniline ($X^- = Cl^{-1}$, HSO_4^-).

Figure 2.
Mechanism of polymerization of aniline.

1962 Mohinler et al. [13] investigated the mechanism of the electrochemical oxidation of aniline in sulfuric acid and deduced that the initial oxidation requires the formation of an aniline radical as shown in **Figure 2**. Where these generated radicals may combine in different ways to form PANI for example head-to-tail coupling or tail-to-tail coupling.

Since 1984 the PANI is being used as an attractive conductive material for the synthesis of conductive composites for variety of practical applications such as electromagnetic shielding, microwave absorption [14–17], static electricity dissipation, heating elements, conducting glues, conducting membrane materials, and paint coatings for anticorrosion property, and sensor materials [18–28]. Among the conducting polymers, PANI is known for having probably the best combination of stability, conductivity and low cost [3]. Despite having versatile use in large scale industrial applications, many of the potential use of PANI yet need to be explored. One of the major drawbacks of PANI is the lack of its processability. The most promising approach to overcome this problem of PANI is the formation of composite with using nonconducting polymers as matrix. Nevertheless, the synthesis method to produce composites with specified characteristics remains number of obstacles that need to be overcome. There are several known methods to synthesis PANI-based composite materials are as follows:
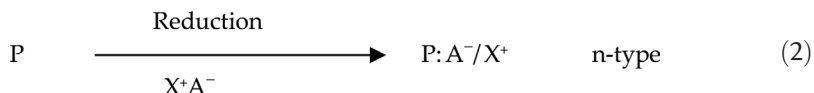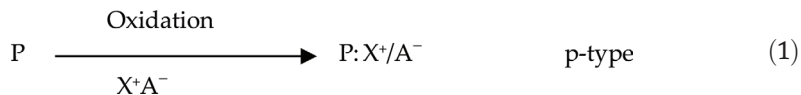
- Chemical in situ polymerization of aniline in a matrix or in a solution with a matrix polymer;

- Dispersion polymerization of aniline in the presence of a matrix polymer in a disperse or continuous phase of a dispersion;

- Emulsion polymerization

- Solution blending soluble matrix polymers

- Dry blending

- Melt processing

Above mentioned methods, each of these methods has its own advantages and limitations. Specifically, the synthetic direction is preferred, as it produces inexpensive conducting composites, because of the use of inexpensive aniline instead of more expensive PANI. The other reason of the use of this method is that it produces composites which have conductivity only in a thin surface layer, have good homogeneity and a low percolation threshold. On the other hand, blending methods are sometimes seemed to be more technologically desirable from the view point of large scale production, particularly in the case of melt procession techniques. It can be concluded that the blending methods will probably become very practicable when techniques to produce inexpensive, nanosized PANI will be developed.

3. Doping and conduction mechanism

Polymers are insulators because of the intrinsic property of the C-C covalent bonds. The primary requirement for a polymer to be conductive it must have a conjugation in chain backbone for easy movement of the charge carriers. Since the single and double bonds are in conjugation with lone pair in PANI backbone but it does not make PANI conductive, unless an intrinsic charge-carriers is developed. Once the charge carriers are generated, the band gap is reduced and system becomes conductive. The charge-carriers are provided extrinsically, typically by a charge transfer process (by partial oxidation or partial reduction with appropriate doping agents), this term generally known as 'doping'. For example, the band gape in saturated polyethylene is about 5 eV and decreases to about 1.5 eV in the fully conjugated system of polyacetylene, hence, their respective conductivities increase from 10^{-17} and 10^{-8} S cm^{-1}. The band theory model describes that the electrical conductivity can be altered by either removal of the electrons from the valence band or by oxidizing agent – creating positive charge, and donation of an electron to the empty conduction band using reducing agent. Doping of the polymers may be done with several techniques such as (a) gaseous doping, (b) solution doping, (c) electrochemical doping, (d) self-doping, and (e) radiation induced doping. Doping can also be achieved by irradiating the polymer by neutrons. However, the conductivity in polymers is associated with charge carriers that do not have free spins, unlike metals. During a donor or acceptor molecule to a conjugated polymer, the reaction takes place is actually a redox reaction and quite different from the doping of metals such as silicon and germanium, where

substitution of atoms take place in the lattice. The term 'doping' is common for both conducting polymer and metals, but it should be noted that the doping of conducting polymers is a result of the formation of a polymer salt and this generally happened either by exposing the polymer to the dopant in solution or by electrochemical process. The general reactions can be expressed as follows - Eqs. (1) and (2):

$$P \xrightarrow[X^+A^-]{\text{Oxidation}} P: X^+/A^- \qquad \text{p-type} \qquad (1)$$

$$P \xrightarrow[X^+A^-]{\text{Reduction}} P: A^-/X^+ \qquad \text{n-type} \qquad (2)$$

where P represents a section of polymer chain. The first step is the creation of a cation (or anion) radical, which is called a soliton or a polaron. This step may then be followed by a second electron transfer with the formation of dication (or dianion) known as bipolaron [29] as can be seen in **Figure 3**. P-type conducting polymers are conventionally used in secondary batteries. These polymers are doped by low molecular weight anions, such as perchlorate, chloride, and tetrafluoroborate ions. Upon reduction, these polymers become neutral by releasing the dopant anions and vice versa they capture the anion upon re-oxidation. It is
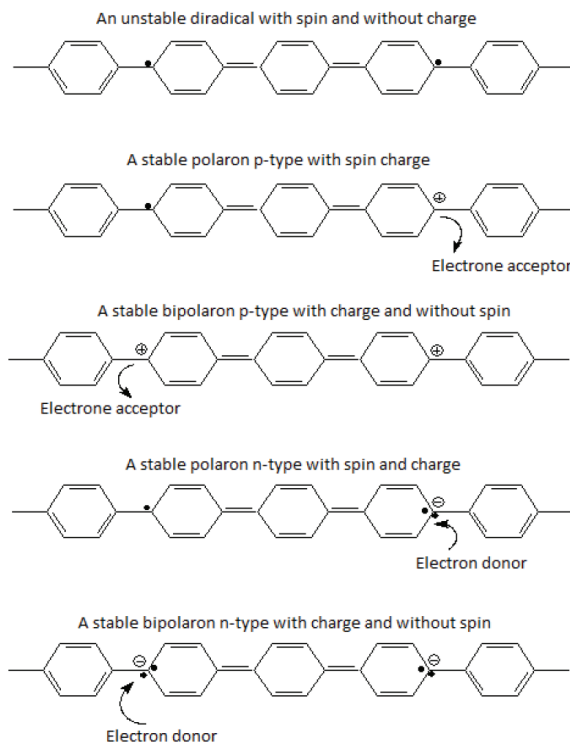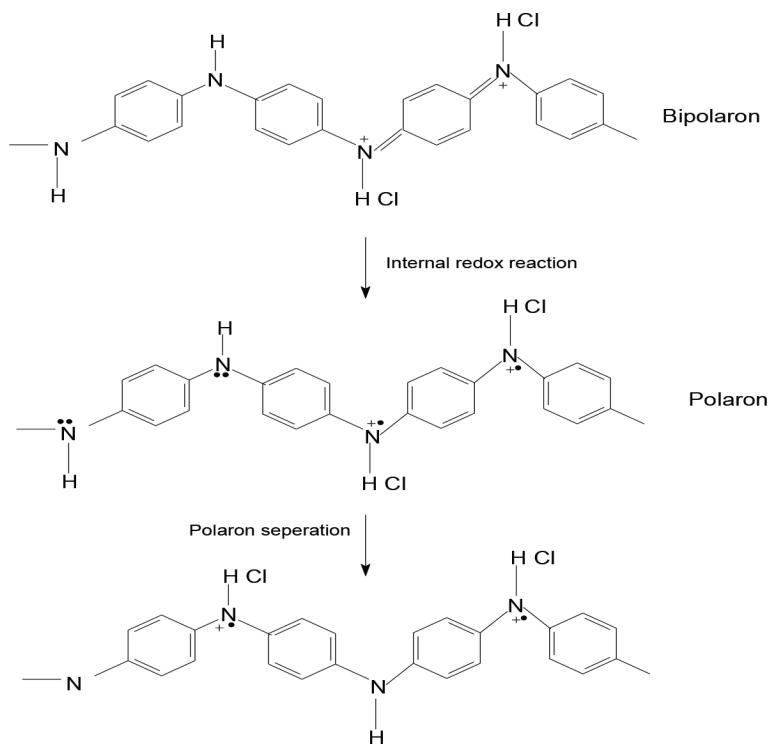

Figure 3.
A schematic diagram of evolution of charge-carriers in the form of polarons and bipolarons in polyphenylene [29].

therefore, charging and discharging characteristics of secondary batteries depends on the diffusion of ions into and out of the polymers. Alternatively, after the first redox reaction, charge transfer complexes may form between charged and neutral segments of the polymer. The reactions between conjugated polymers and oxidants (p-type doping by an acceptor) or reductants (n-type doping by a donor) have been observed to cause a dramatic increase in electrical conductivity. When doped with protonic acids, the imine N in PANI gets protonated. This is because of the higher basicity of the imine N as compared to the amine N. One of earlier surprises associated with PANI was the fact that it can be doped by protons, which doesn't change the π-electron count of the system. However, this mystery is now resolved by a very popular two-step model, for example, in case of polyphenylene and polyaniline [30]. The emeraldine base of APNI consists two amine nitrogen atoms followed by two imine nitrogen atoms and is a blue color insulating form of PANI. This form can be transformed into a conducting form of PANI called as emeraldine salt. Two different process are generally used to make emeraldine salt a green color product (1) protonic acid doping and (2) oxidative doping. Protonic acid doping corresponds to the protonation of the imine nitrogen atoms without electron exchange. While in oxidative doping, emeraldine base goes through several stages with electron exchanges.

Dopant concentration also does effect on number of spins and electrical conductivity of the conducting polymer. The initial protonation of the two imine N gives rise to a doubly charged bipolaron, the bipolaronic structure then spontaneously dissociates to give two polarons (radical cations). In later step, the polarons separate to yield a polaron lattice. The polaron lattice resembles the fully reduced leucoemeraldine form of polyaniline, but for the alternate amine N atoms that are robbed of an electron. Similarly, the bipolaronic structure is formed by oxidative doping of the adjacent N atoms, which is followed by coupling of lone electron on N to form an extra bond (**Figure 4**). Thus, oxidative doping of the leucoemeraldine base provides a viable route to the charge carriers in the PANI segments [31]. The polarons and bipolarons are mobile under the influence of electric field and can transport along the chain. The conduction mechanism is believed to involve polaronic carriers i.e. the protonated emeraldine which consists of a delocalized poly (semiquinone radical cation). By this way the most conductive form can be approached through two different process—protonic acid and oxidative doping. Protonic acid doping of emeraldine base segment with HCl results in protonation of the imine nitrogen atom in the chain backbone and give emeraldine salt form (**Figure 5**). According to magnetic theory, if the protonated emeraldine base has dication (bipolaron), it should show diamagnetism property, however it shows a paramagnetic characteristic, because of a poly-semiquinone radical cation – one resonance form consisting of two separate polarons. Some common oxidizing agents (p-type dopant) are $HClO_4$, $FeCl_3$, AsF_5, I_2, NH_4BF_4, SO_3CF_3, HCl, HNO_3, H_2SO_4, H_3PO_4, and some reductants are Li, K, Na, etc. By this way the highly conductive doped form of.

As mentioned earlier, doping is a multi-steps process involving electron removal from polymer chain segments leading to the generation of charge carriers. The charge-carriers in the form of radical cations (p-type) or radical anions (n-type) are thus produced on the polymer chains, which are called polarons (with spin) and bipolarons/solitons (spinless). Doping allows electrons to flow due to the formation of conduction bands, that makes PANI conductive. As doping occurs, the electrons in conjugation are able to jump around the polymer chains. In general, "doping is the act of adding a small amount of impurity (the dopant) to a material to alter its properties" [32, 33]. The presence of a heteroatom (nitrogen) in the conjugated path of PANI chain provides a way to dope PANI through non-redox routes and

Figure 4.
The two-step model that describes the disproportionation of a bipolaron to a pair of polarons in proton doped PANI [31].
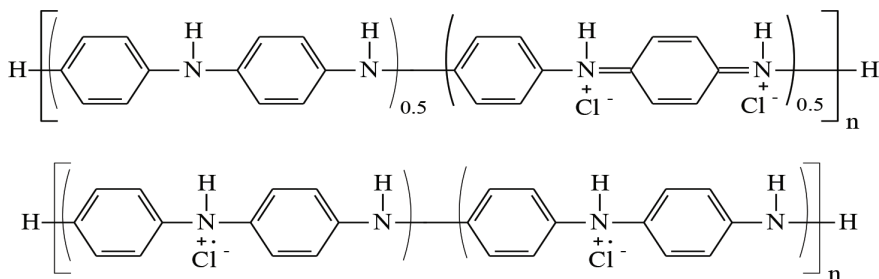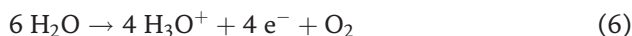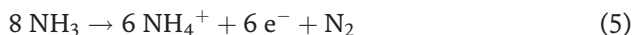

Figure 5.
Chemical structure of emeraldine salt [31].

have significant influence on the nature of the quasi-particles which are responsible for charge transport. The doping can be carried out by reacting PANI with an acid (HNO_3, HCl, H_2SO_4) that pulls out the lone-pair of electrons from the double-bonded imine N atoms and thereby creating vacancies in the π-electron cloud [34–37]. This is fundamentally different from the analogues of polyacetylene, where the doping cannot be associated with a particular atomic site. This converts the imine (nitrogen with a double bond) sites to iminium (an imine with a positive charge) sites. X^- (NO_3^-, Cl^{-1}, HSO_4^-) is the conjugate base of the acid used to dope PANI. Similarly, PANI may also be doped by using organic dopant like para-toluene sulfonic acid (p-TSA), camphor sulfonic acid (CSA) and dodecyl benzene sulfonic acid DBSA [36], example is given in **Figures 7** and **8**. A general equation for doping of a conjugated polymer may be given by the following chemical reactions – Eqs. (3) and (4):

$$P + 2FeCl_3 \rightarrow P^+ : FeCl_4^- + FeCl_2 \tag{3}$$

$$P + Na \rightarrow P^- : Na^+ \tag{4}$$
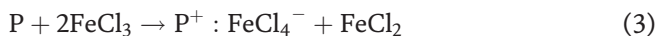
Another important aspect of doping is its reversal, called dedoping or compensation or electrical neutralization of a doped polymer in which, for example, a p-type doped polymer reacts with some reducing agents and regains its insulating state. The dedoping agent, diffuses into polymer matrix and neutralizes the charge of the system by a charge-transfer reaction. This process may involve chemical reactions between the dedoping agent and carbonium ion or/and dopant leading to the neutralization by charge-transfer. This process is fully reversible as doping and dedoping can be repeatedly performed by exposing PANI to acid and base, respectively, as shown in **Figure 6**. The change in resistance from the dedoped to the doped form is easily measured electronically, making polyaniline an excellent sensor for acids and bases. The generally used dedoping agents for p-type doped conjugated polymers are ammonia, water, hydrazine, etc. and the chemical reaction for the process may be given by the following Eqs. (5)–(7):

$$8\,NH_3 \rightarrow 6\,NH_4^+ + 6\,e^- + N_2 \tag{5}$$

$$6\,H_2O \rightarrow 4\,H_3O^+ + 4\,e^- + O_2 \tag{6}$$

$$P^+ + e^- \rightarrow P \tag{7}$$

The overall doping and dedoping with acid halide can be expressed as follows:

Dedoping may also be effected by thermal treatment of doped-PANI with acid halide and camphor sulfonic acid dopants (PANI-HCl and PANI-CSA) under ambient condition, as shown **Figures 7** and **8** [36–38]. Kinetics of dedoping may be studied by several methods, i.e. electrical conductivity measurements, X-ray diffraction, optical spectroscopy etc. which may be interpreted into the depletion of the extent of doping. Doping may also be processed by radiation in which the locally oxidized chain is reduced by photo-absorption and in result an electron-hole pair creates. High energy radiation such as γ-rays, electron beam, and neutron radiation may be used.

Doping causes significant restructuring of the geometry of polymer. Apart from the changes in bond lengths, the six membered rings also rotate to a more planar configuration, thereby increasing the wave function overlap to make the electron state more delocalized. Dedoped PANI is an insulator with a 3.8 eV band gap, on doping, the conductivity changes by 10–12 orders of magnitude. There are several debatable issues pertaining to the nature of the charge carriers, dimensionality of
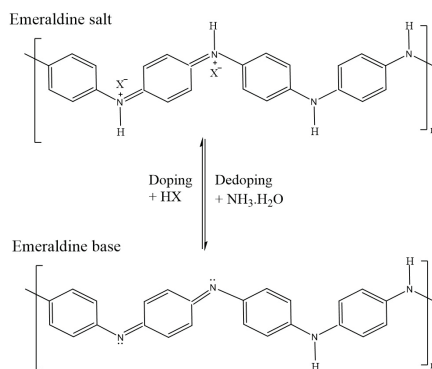
Figure 6.
*Doping and dedoping chemistry of PANI [34].*
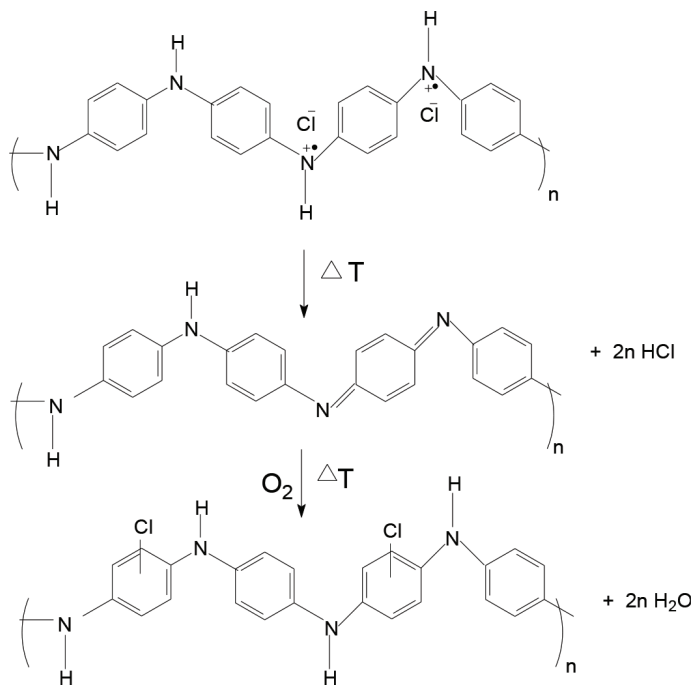
Figure 7.
Dedoping process in PANI-HCl [36].
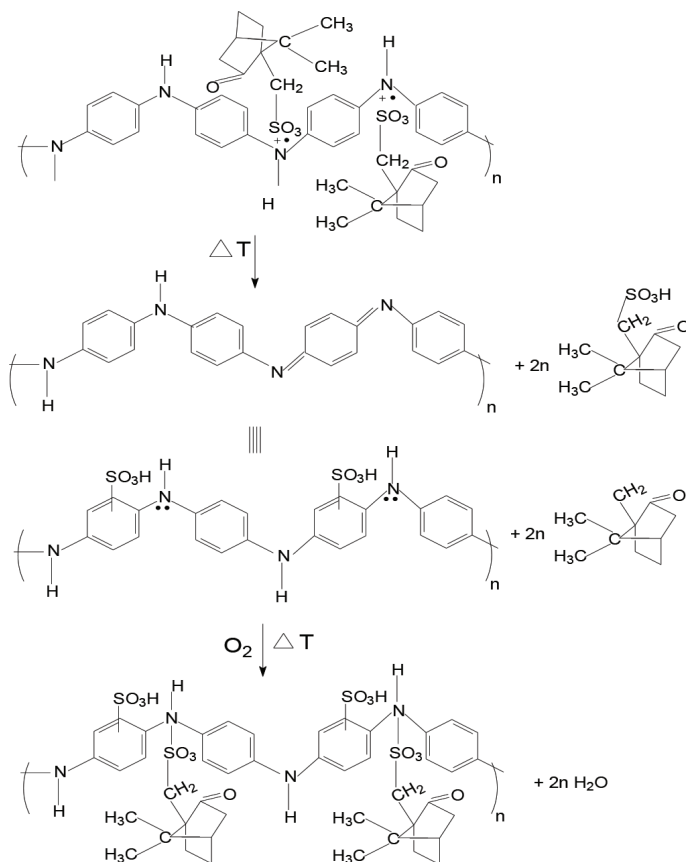
Figure 8.
Dedoping process in PANI-CSA [36].

the conducting state and the effect of disorder on the charge transport in doped PANI. Over the years, a great deal of experimental and theoretical endeavor has been put to understand these fundamental issues. A lot of questions are still lying unanswered. PANI can occur in a number of well-defined different oxidation states as shown in **Figure 9** [39]. There are several known oxidative states of PANI ranging from fully reduced leucoemeraldine to partially reduced protoemeraldine, and partially oxidized forms emeraldine and nigraniline to the fully oxidized form pernigraniline. Unlike other polyaromatics, PANI's oxidized states are insulating, unless the charge carrier and proton is generated in particular partially oxidized form (emeraldine) of PANI, this process, typically knows as 'protonic acid doping' [40]. The oxidation states of PANI can be induced through doping with oxidizing agents such as iodine, cerium(IV) sulfate, and potassium dichromate, however the obtained electrical conductivity is lower than that that of protonic acid doping [41–45]. The conduction mechanism in PANI is due to the polaronic carrier that is protonated emeraldine form of PANI, which involves the delocalization of poly-semiquinone radical cation.

Furthermore, the electronic state of PANI can also be altered through electro-chemical diffusion of dopant ions (also called as electrochemical doping) in the polymer unites. This process can be done by applying a proper voltage between two electrodes via a potential loading device to cause a reverse electrode reaction in electrolyte solution. McManus et al. [46] reported the electrochemical doping of polyaniline using phthalate buffer solution and suggested that polyaniline can be reversibly doped into three forms: (i) closed valence-shell reduced form, (ii) a radical cation intermediate form, and (iii) a closed valence-shell oxidized form. And they found the conductivity highest for an intermediate range of oxidation during electrochemical doping polyaniline also changes the absorption spectra. Recently, the replacement of sulfate ion by Cl^- and ClO_4^- via electrochemical method [47]. Electrochemical doping is not limited to polyaniline but also can be observed other

leucoemeraldine

protoemeraldine

emeraldine

nigraline

pernigraline
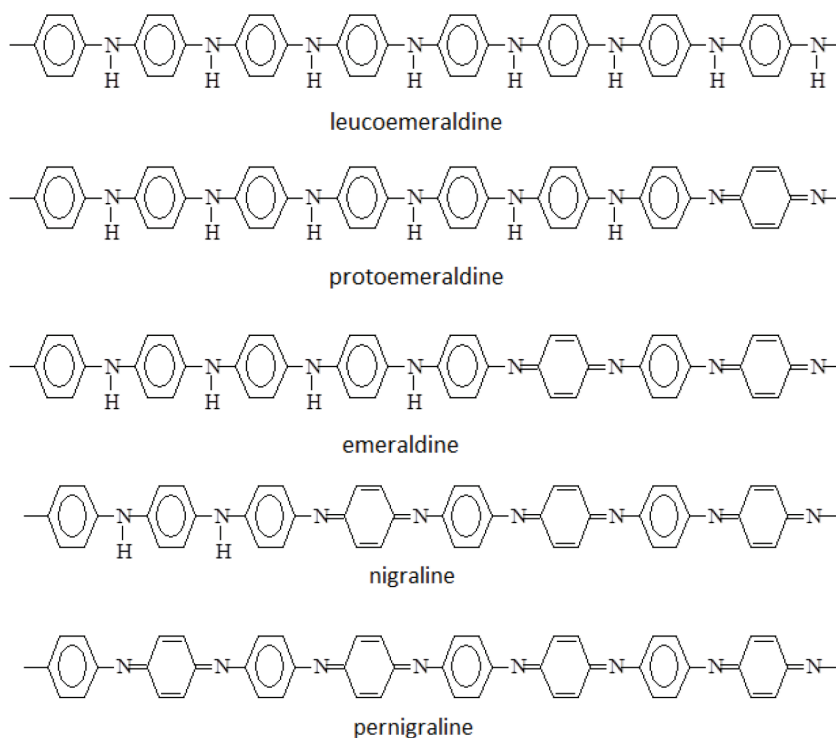
Figure 9.
Different oxidation states of polyaniline [39, 44].

conducting polymers for example, Gennies and Pernaut [48] have demonstrated that the diffusion coefficient of ClO_4^- into and out of the electrodeposited films of polypyrrole (PPy). The electrochemical redox reaction follows the Nerstian relation and the diffusion coefficient value of 6.0×10^{-10} cm^2 s^{-1} was calculated at 298 K in 0.5 M $LiClO_4$/acetonitrile electrolyte solution. The relationship with the variation in $LiClO_4$ concentration in the electrolyte and the value for doping is slightly lower than that for undoping processes at 298 K. A model for time-dependence of concentration relaxation of holes S^+, Li^+ and ClO_4^- has been suggested for diffusion during doping and undoping processes. Authors proposed that the diffusion involves the concentration relaxation of all three species simultaneously to maintain electroneutrality in the system. The diffusion coefficients for small dopants varies from 10^{-5} to 10^{-18} cm^2 s^{-1} [49–51]. Abalyaeva et al. [52] used a combination of voltabsorbometry and chronoabsorbometry to estimate the coefficient of BF_4^- diffusion into 0.49 μm thick film of polyparaphenylene produced by vacuum evaporation and a value of 5.0×10^{-9} cm^2 s^{-1} was found. Stamm [53] estimated a value of 3.0×10^{-6} cm^2 s^{-1} for AsF_5 diffusion into oriented fibers of polyparaphenylene produced by solid-state extrusion technique.

The water content is also does effect in the conductivity of the conducting polymer. The conductivity is affected by the water content as completely dry samples are five times less conductive than the samples containing some water [54]. The emeraldine base is soluble in N-methyl-pyrrolidone [55], but protonated polyaniline is insoluble in organic solvents and only soluble in aqueous acids. Substitution of aniline monomer with alkyl or alkoxy groups improves the solubility in organic solvents but has a negative influence on the conductivity [56–58]. The position of the substituent also has an influence on the polymerization. The ortho- and meta- isomers give the same polymer, but the reactivity of the meta- isomer is considerably lower, resulting in a lower yield.

4. Conclusion

The doping concept in conducting polymers is a unique and play central role to enhance the conductivity which distinguish them from other ordinary polymers. The doping mechanism in polyaniline holds especial representation among all conducting polymers due its unique oxidation states. In the light of aforementioned observation, the basic concept of polyaniline synthesis, doping and conduction mechanism permits in-depth exploration not only for fundamental scientific interest but also further technological applications.

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