3.3 Conducting Polymer-Polyaniline(PANI):

PANI is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black [2]. Surville et al [3] in 1968 reported proton exchange and redox properties with the influence of water on the conductivity of PANI. In 1911 Mecoy and Moore [4] had suggested electrical conduction in organic acids. However, interest in PANI was generated only after the fundamental discovery in 1977 that iodine doped polyacetylene has a metallic conductivity. PANI as a chemical substance has been known for long time [5-6].

At the beginning of the 20th century organic chemists began investigating the construction of aniline black and its intermediate products [7]. Wills Tatter and co-workers in 1907 and 1909 regarded aniline black as an eight-nucleus chain compound having indamine structure [Fig. 3.1].

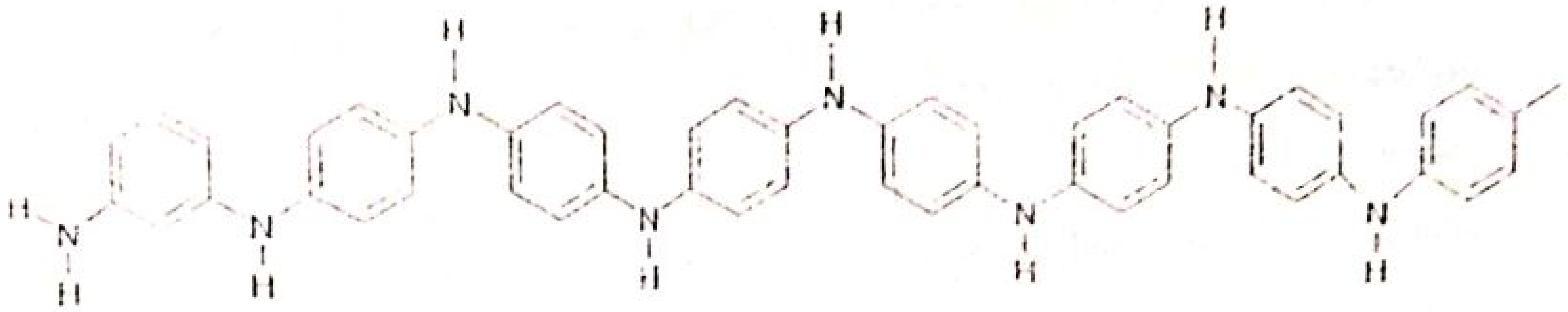

Fig. 3.1: Indamine Structure

However, in 1910-12 Green and Woodhead [8] were able to report various constitutional aspects of aniline polymerization The conclusions of their study were as follows

- There are four quinoid stages derived from the parent compound leucoemeraldine
- The minimum molecular weight of these primary oxidation of anilines are in accordance with an eight-nucleus structure
- The conversion of emeraldine into nigraniline consumes one atom of oxygen
- The conversion of emeraldine into pernigraniline consumes two atoms of oxygen
- The conversion of nigraniline into pernigraniline consumes one atom of oxygen
- The reduction of emeraldine to leucoemeraldine consumes four atoms of hydrogen
- The reduction of nigraniline to leucoemeraldine consumes six atoms of hydrogen
- The reduction of pernigraniline to leucoemeraldine consumes eight atoms of hydrogen

These authors carried out oxidative polymerization studies using mineral acids and oxidants such as persulphate dichromate and chlorate and determined the oxidation state of each constituent by redox titration using $TiCl_3$. They also extended their studies on the oxidative polymerization of o- and p- chloroaniline and o-anisidine and reported that dimethylaniline remained unattacked under these experimental conditions

This triggered research interest in new organic materials in the hope that these would provide new and/ or improved electrical, magnetic, optic material or devices

The hope was based on electronic structure and the combination of metal like or semiconducting character with the processibility and flexibility of classical polymers and, above all, the ease with which structural modification can be carried out via synthetic organic chemistry methodologies. Among the conducting polymers, PANI has been the most widely studied as a exclusive member for the conducting polymer family for the following reasons

- Easy synthesis.
- It is the only conducting polymer whose electronic structure and electrical properties can reversibly be controlled by both oxidation and protonation.
- It has interesting electrochemical behaviour
- It shows environment stability
- Ease of non-redox doping by protonic acids.

3.4 Structure of Polyaniline:

The protonation and deprotonation and various other physico-chemical properties of PANI can be said to be due to the presence of the -NH- group. The general structure of PANI can be shown above in Fig. 3.2

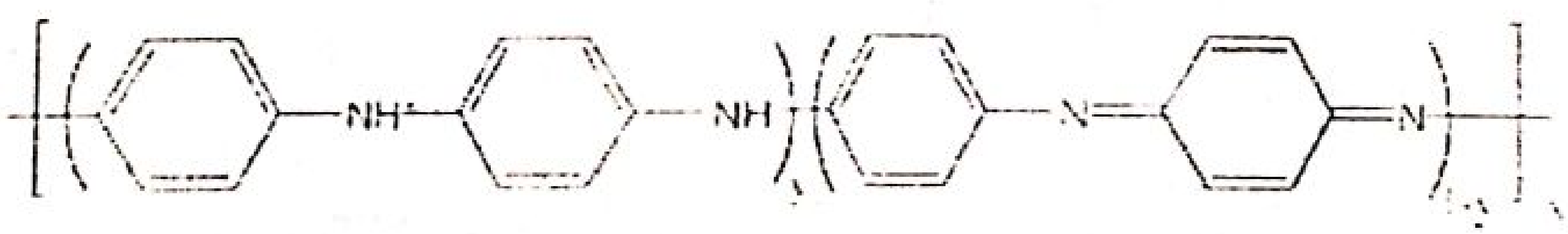

Figure 3.2-General structure of PANI [1]

Green and Woodhead [5] were the first to depict PANI as a chain of aniline molecules coupled head-to-tail at the para position of the aromatic ring. They have proposed a linear octameric structure for PANI. Polyaniline, a typical phenylene based polymer, has a chemically flexible –NH – group in the polymer chain flanked by phenyl rings on either sides. The diversity in physicochemical properties of PANI is traced to the –NH– group. Out of several possible oxidation states, the 50 % oxidized emeraldine salt state shows electrical conductivity [8-9]

In combination with comparable results obtained with other similar polymers such as PPy and PTh, PANI have caused a rapid increase in experimental investigations into the mechanism and kinetic of the formation, molecular structure electro-optical and believable application [10]

Table 3.1. : Raman assignments of PANI [11]

Frequencies (cm^{-1})	Assignments
1160–1180	C–H bending
1230–1255	C–N stretching
1317–1338	C–N′ stretching
1470–1490	C=N stretching
1515–1520	N–H bending
1580	C=C stretching
1600–1620	C–C stretching

3.5 Conductivity of PANI:

As mentioned below, PANI exists in three oxidation states (leucoemeraldine, emeraldine and pernigraniline forms) that differ in chemical and physical properties [12]. Only the green protonated emeraldine has conductivity on a semiconductor level of the order of 10^0 S cm-1, 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). Protonated PANI converts to a non-conducting emeraldine base when treated with alkali solutions (Fig 3.3) [13]

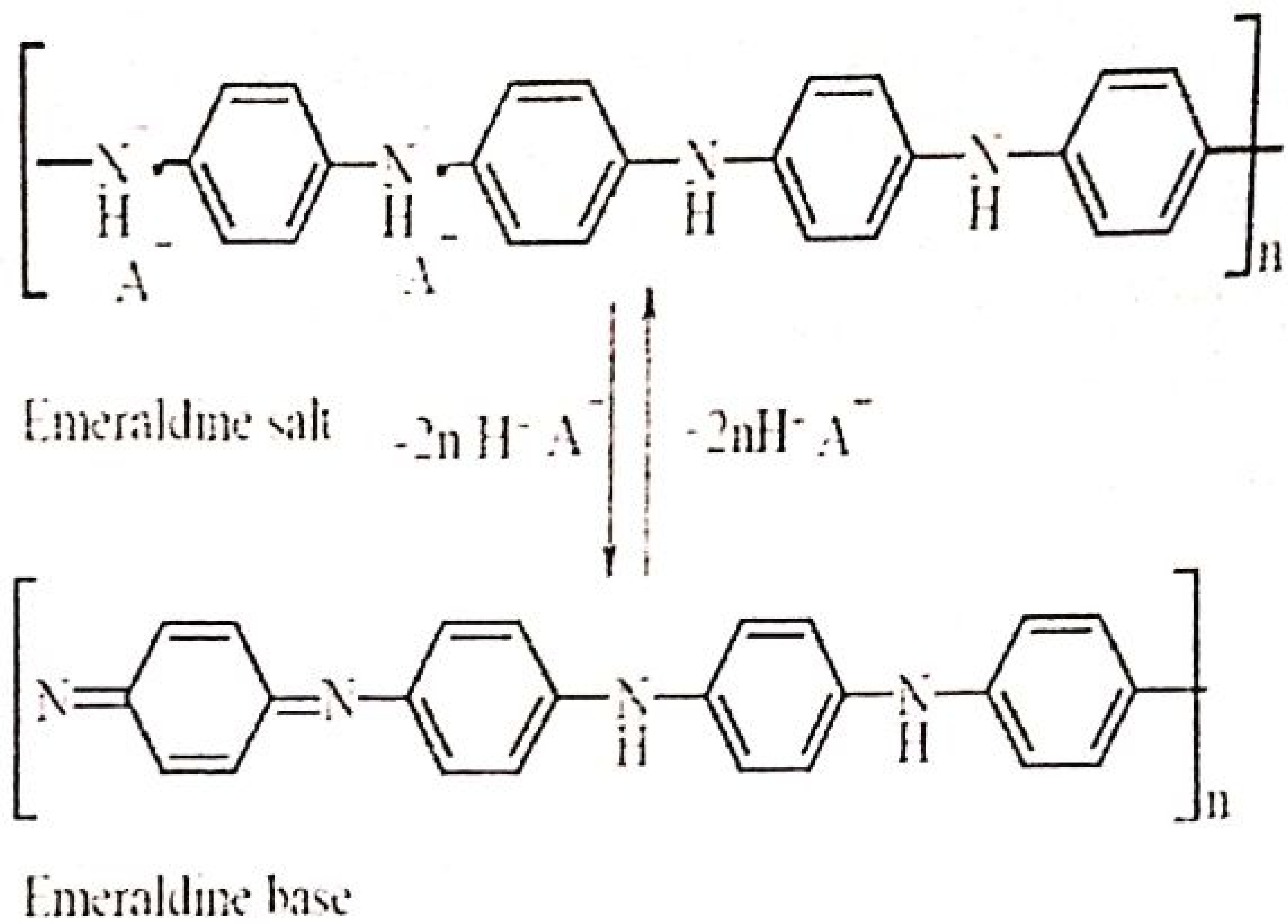

Figure 3.3: Emeraldine salt is protonated in the alkaline medium to emeraldine base. A- is arbitrary ion, e.g., chloride

The conductivity of PANI can be changed by doping, and spans a very wide range ($<10^{-12}$ to 10^{5} S cm-1) depending on the level of doping [14]. The changes in physicochemical properties of PANI occurring in response to various external stimuli are used in various applications, e.g., in sensors and actuators [15]. Other uses are based on the combination of electrical properties typical of semiconductors with materials properties characteristic of polymers, like the development of "plastic" microelectronics, electrochromic devices. The establishment of the physical properties of PANI reflecting the conditions of preparation is thus of fundamental importance [16]. Polyaniline (PANI) and poly (ethylene dioxythiophene) (PEDT) have a much higher conductivity and stability, combined with a low absorption as compare to alkoxy-substituted polythiophenes. It is postulated that, this is due to the fact that the doping process in these materials is different, involving no shifts in absorption peaks and leading to low-lying near IR absorption bands at less than 0.6eV [17]. During the course of polymerization reaction, these cations of intermediate stability dimerize, and further radical coupling reaction leads to the formation of green PANI [18].

3.9 PANI doping:

The PANI must be doped if associated to electronic conducting polymers. The term "doping" is employed here by analogy with semiconductors like silicon or germanium in which atoms like phosphorous or boron are introduced. Conducting polymer doping consists to insert into the polymer, electron acceptor molecules (oxidation) or electron donor molecules (reduction). The obtained polymer is then considered as a p-type or n-type one, respectively.

PANI is a specific conducting polymer because of its conducting mechanism induced either by the oxidation of the polyleucoemeraldine base or by the protonation of the polyemeraldine base. The two routes are shown in Fig 3.12

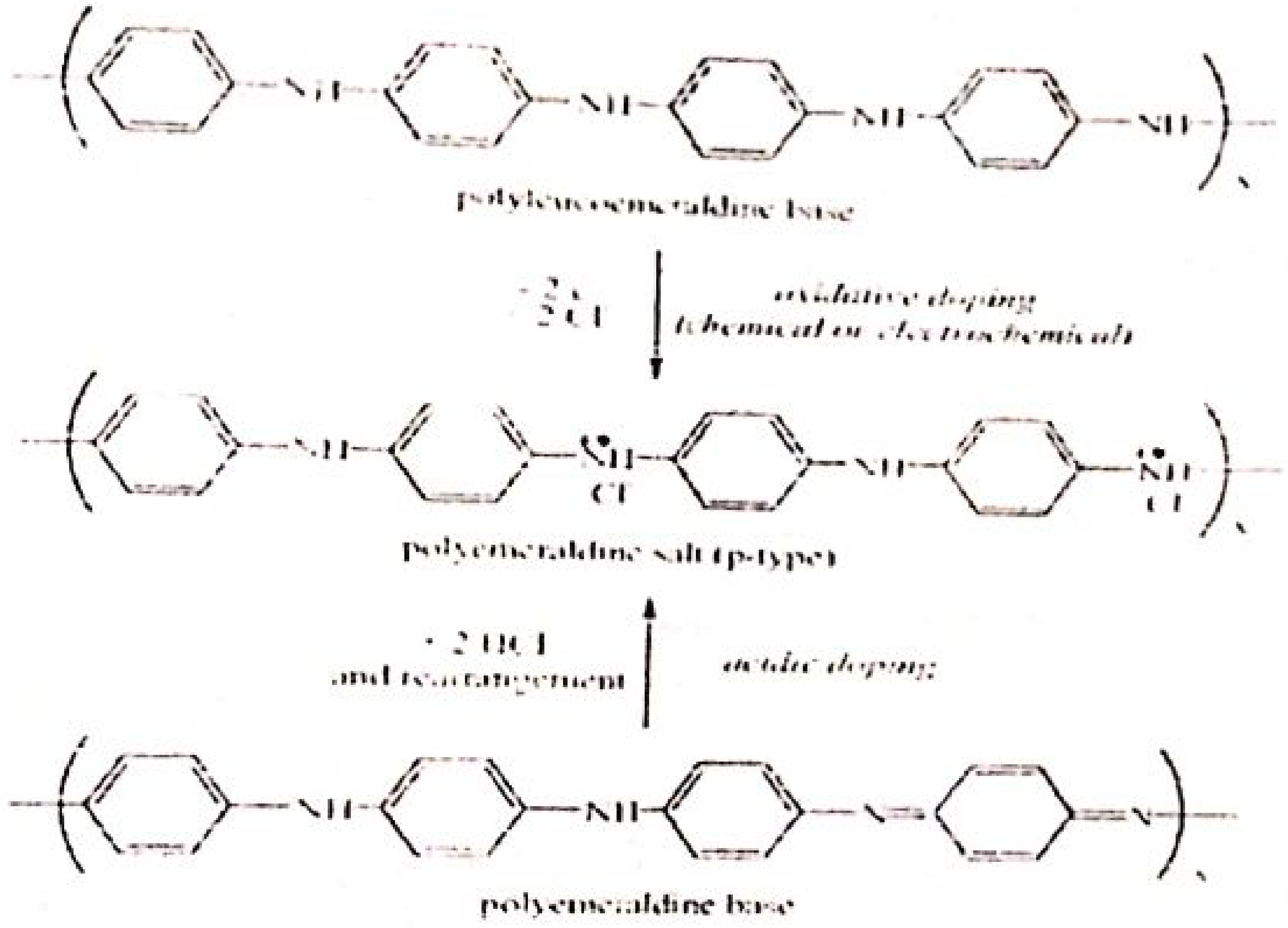

Figure 3.12:-Doping mechanisms of PANI

3.9.1 Oxidative doping:

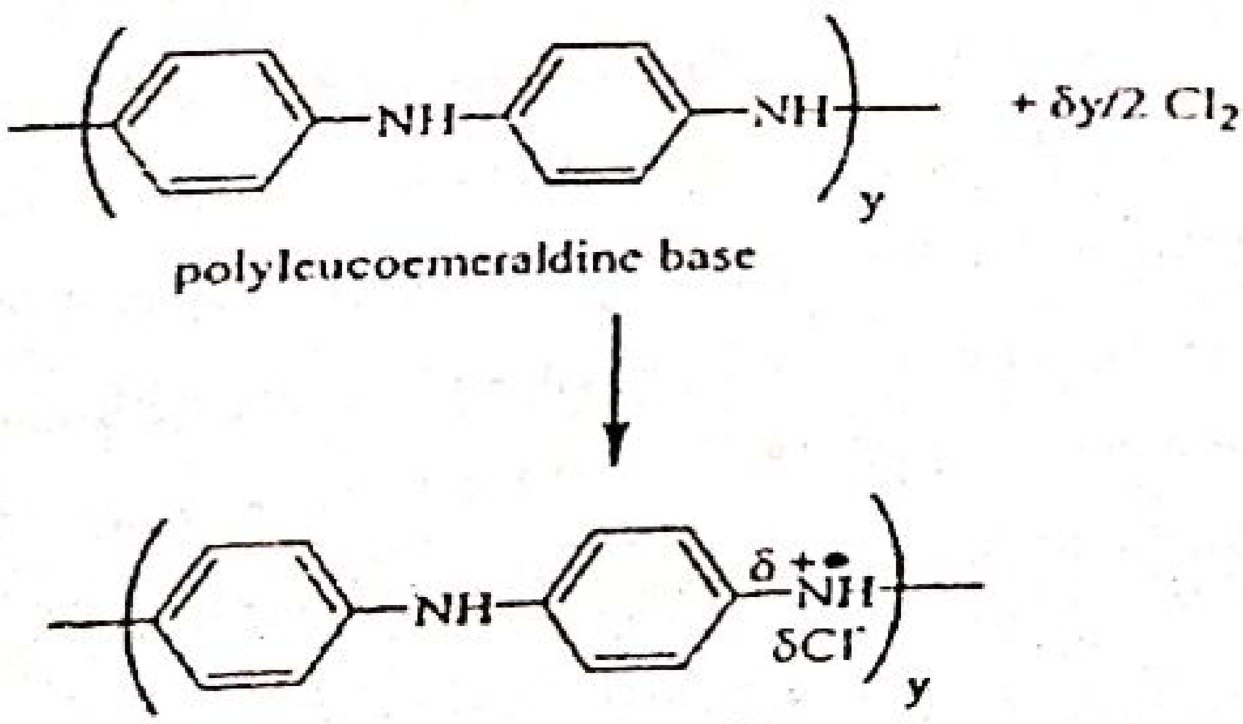

Figure 3.13 (a) Oxidative doping with Cl_2

The oxidative doping is realized through chemical or electrochemical processes from the totally reduced form of PANI, polyleucoemeraldine base as shown in Fig. 3.13

indicates a way of polymer synthesis. Polyleucoemeraldine base is prepared by reduction of polyemeraldine salt with phenylhydrazine or hydrazine solutions by dipping for 5 or 6 min [39] The chemical oxidative doping is run either with a chlorine or a less toxic iodine agents in a carbon tetrachloride solution, or with $(NO)^{+}(PF_6)^{-}$, $FeCl_3$ or $SnCl_4$ organic solutions, or with oxygen or hydrogen peroxide in an aqueous acidic solution. The following examples illustrate the oxidative doping with Cl_2 Fig 3.13 (a) and also with H_2O_2 in an acidic solution HA (Fig. 3.13(b)).

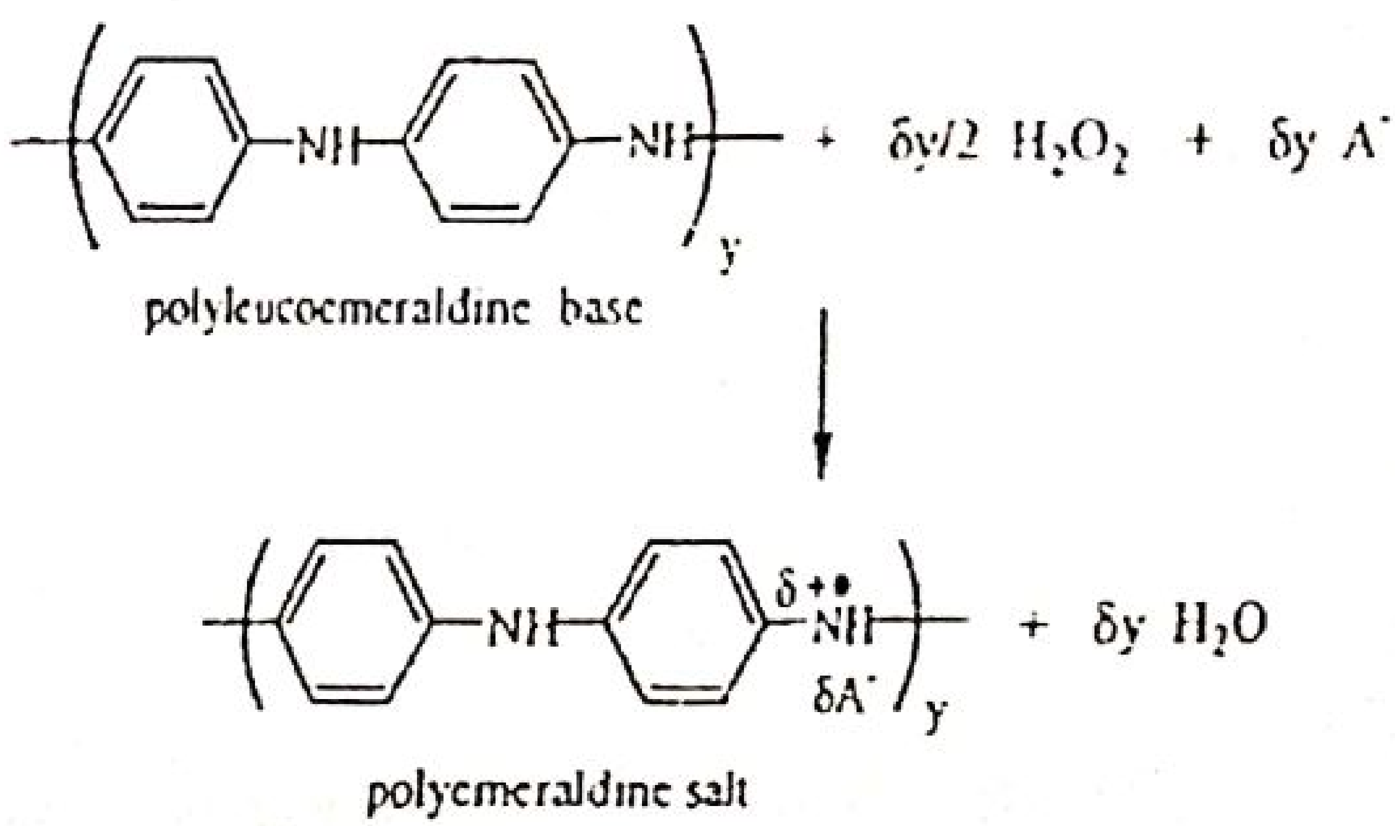

Figure 3.13 (b) Doping with H_2O_2 in an acidic solution HA:

In the latter case, the nature of the counter-ion A^- (Cl^-, HSO_4^-, $H_2PO_4^-$) is controlled. When Cl_2 is considered both as the oxidant and the dopant, H_2O_2 only oxidizes PANI doped with the acidic solution. Although chemical doping is a straightforward and well-organized process, but the control of the doping level δ is difficult. Electrochemical doping solves this problem since the doping level is determined by the voltage applied between the conducting polymer and the counter Electrode [40]. The electrochemical doping of polyleucoemeraldine base can be written as Fig. 3.14:

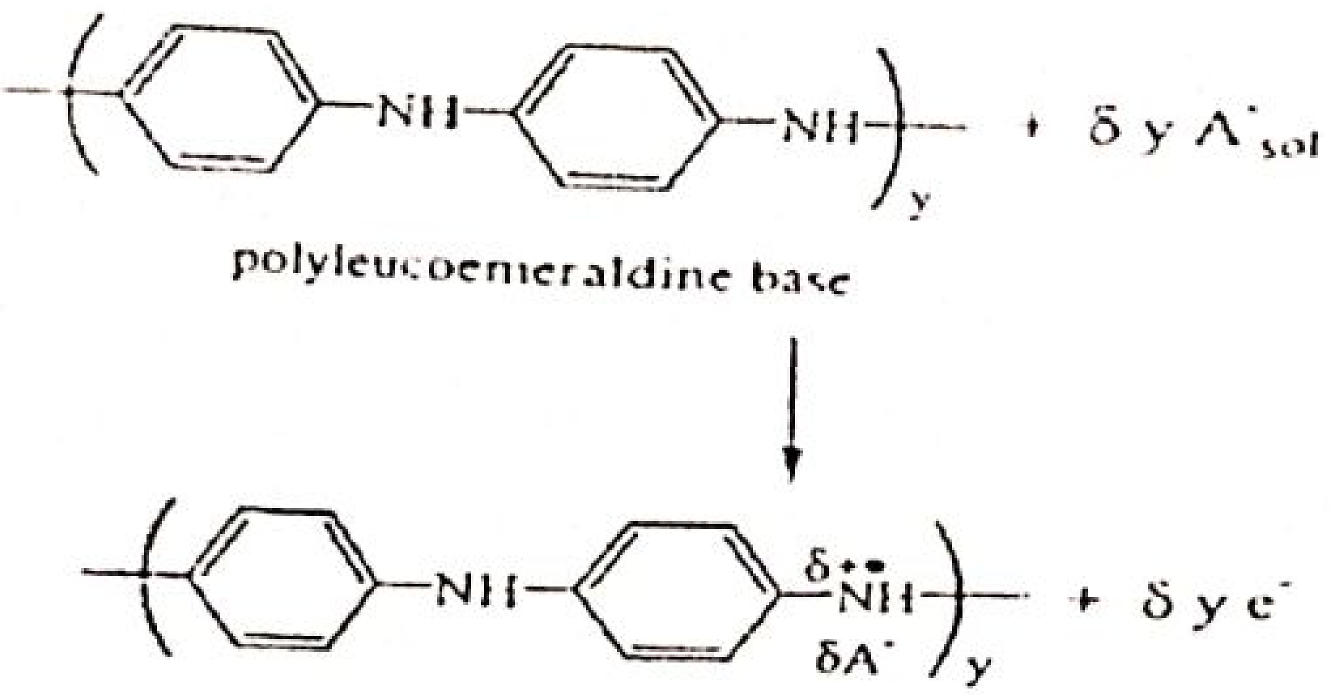

Figure 3.14: Electrochemical doping of polyleucoemeraldine

The counter-ions A⁻ of the electrolytic solution are inserted in the polymer backbone

3.9.2 Acidic doping:

The acidic doping is a exceptional doping case, where no change of the number of electrons associated with the polymer backbone occurs. The acidic doping consists to treat the emeraldine base with a strong acid (HCl, H_2SO_4) that induces the protonation of the imine sites to give the polyemeraldine salt, through a mechanism illustrated in Fig 3.15.

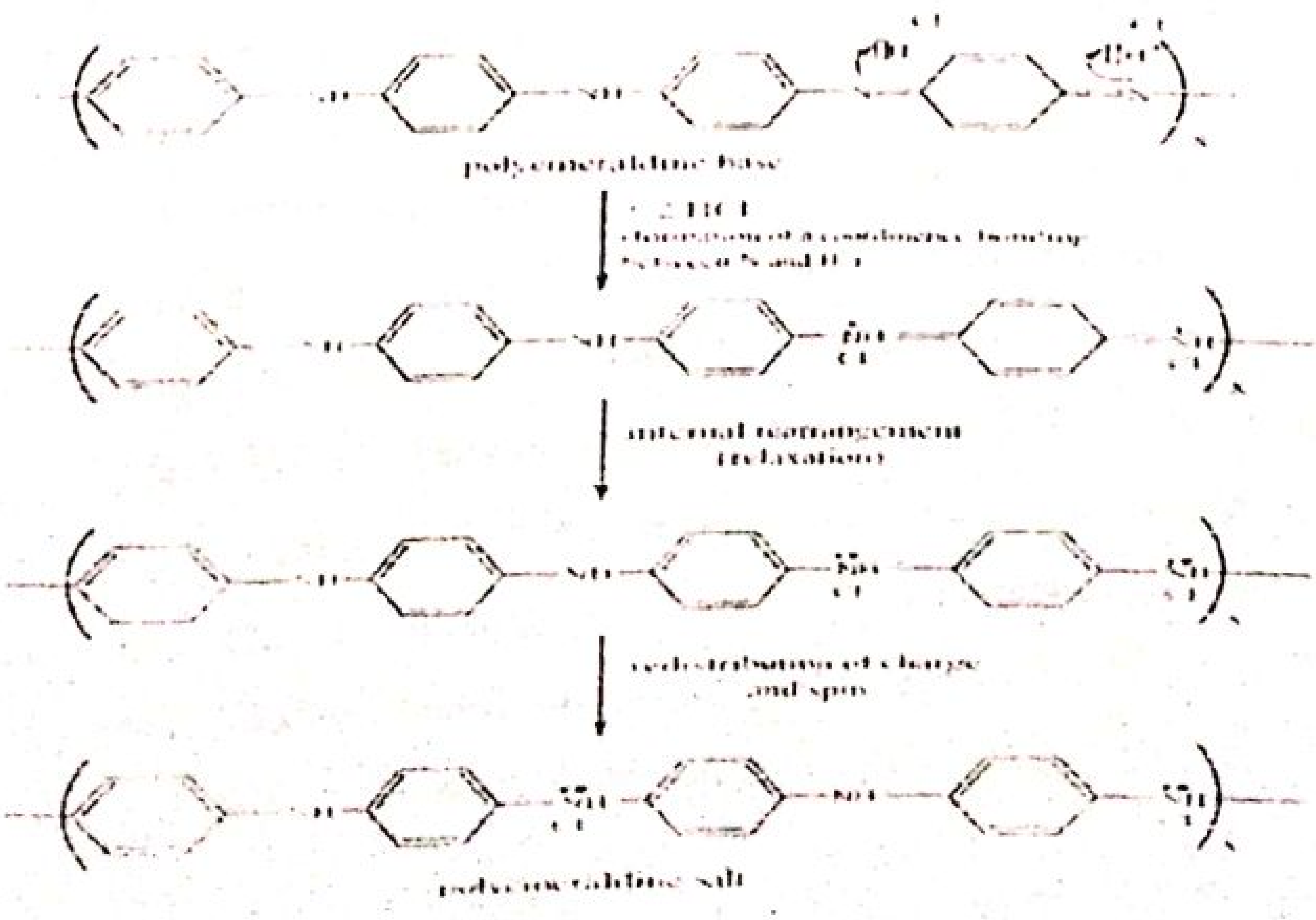

Figure 3.15: Mechanism of acidic doping

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