

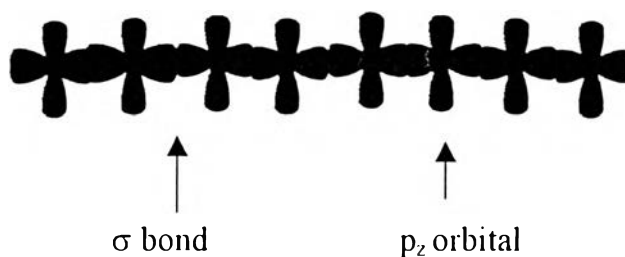
# CHAPTER 1

## INTRODUCTION

### 1.1 Electrically Conductive Polymers

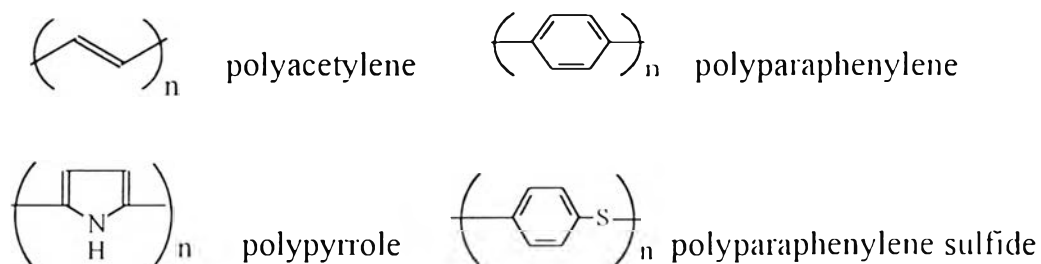
#### 1.1.1 Basic Concepts

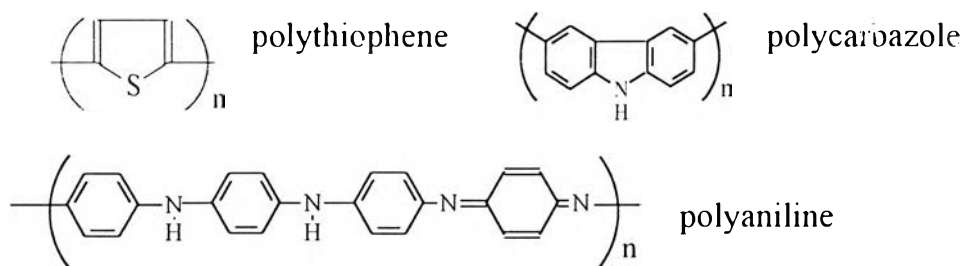
The common electronic feature of conductive polymers is a  $\pi$ -conjugated system which is formed by the overlap of carbon p-orbital and alternating carbon-carbon sigma bonds (Skotheim, 1986) as shown below:



**Figure 1.1** Schematic view of the carbon backbone of trans-polyacetylene chain shows  $\sigma$  bonds overlap of  $sp^3$  orbital of adjacent carbon atoms and  $p_z$  orbital which form  $\pi$  and  $\pi^*$  bands, responsible for the electronic properties of the semi-conducting and metallic states.

The chemical structures of the most through studied members of the conductive polymer family are shown in Figure 1.2:





**Figure 1.2** Repeat units of several electrically conductive polymers.

All of the conjugated polymers shown in Figure 1.2 have chemical structures characteristic for semiconductors; the highest occupied molecular orbital of monomer forms the occupied  $\pi$ -band (valence band) and the lowest unoccupied molecular orbital of the monomer forms the unoccupied  $\pi^*$ -band (conduction band) (Salaneck, 1993).

The conductivity of the pristine (undoped) polymer is transformed from an insulating form to a metallic form by a process called “doping”. Doping introduces a new dopant energy level into the band gap; conduction is facilitated and the electrical conductivity is strongly dependent on the doping level as donor or acceptor species are incorporated. The dopants used to induce an insulator-metal transition in electronic polymers can be both n-type (electron donating) or p-type (electron acceptor). Dopant atoms are positioned interstitially between chains and donate charges to or accept charges from the polymer backbones (Baeriswyl, 1992).

### 1.1.2 Concept of Doping

Doping converts organic polymers from the insulating or semiconducting forms with low conductivity, in range  $10^{-10}$  to  $10^{-5}$   $\text{Scm}^{-1}$ , to conductive polymers ( $1$  to  $10^4$   $\text{Scm}^{-1}$ ) (Salaneck, 1993). The process can be reversed to produce the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes involving dopant counter ions which act to stabilize the doped state, maybe carried out

chemically or electrochemically. The conductivity of the polymers can be controlled by controlling the doping level during the doping process. This permits the optimization for the best properties in each type of polymers. This permits the optimization of properties in each type of polymer.

The prototype conductive polymer, polyacetylene, discovery in 1977 (James, 1980) can be doped either p-doped or n-doped, chemically or electrochemically. The development in the field of conductive polymers has continued to accelerate at a rapid rate and a variety of other conductive polymers and their derivatives have been discovered (Skotheim, 1986).

In the undoped state, the polymer may have a conjugated backbone such as in trans-polyacetylene or in a non-conjugated chain, as in polyaniline emeraldine base. Both polymers will become conjugated, consisting of a delocalized  $\pi$ -system in the doped state (Salaneck, 1993).

The doping process can be divided into 3 types:

1. Redox doping involving dopant ions
2. Redox doping involving no dopant ions
3. Non-redox doping

#### 1. Redox doping involving dopant ions

The redox process involves a change in the number of electrons associated with the polymer backbone. This doping type undergoes either p- or n- redox doping by chemical or electrochemical processes.

##### *-Chemical and electrochemical p-doping*

P-doping involves the partial oxidation of the  $\pi$  electrons in the polymer backbone resulting in a decrease of the number of electrons. P-doping was first discovered by treating trans-polyacetylene with an oxidizing agent such as iodine (Salaneck, 1993):



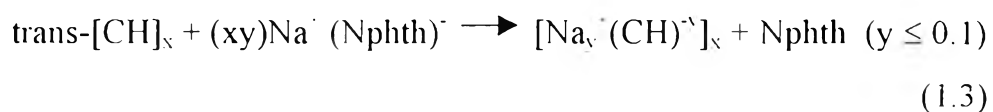
The electrical conductivity of polymers doped with this process can increase from  $10^{-5}$  to  $10^3$  S/cm.

P-doping can also be accomplished by an electrochemical anodic oxidation: by immersing a trans-[CH]<sub>x</sub> film in a solution such as LiClO<sub>4</sub> dissolved in propylene carbonate, and attaching it to the positive terminal of a DC power source, whereas the negative terminal is attached to an electrode also immersed in the solution (Salaneck, 1993).



*-Chemical and electrochemical n-doping*

N-doping is the partial reduction of the  $\pi$ -electron system on the polymer backbone. This type of doping was discovered by treating a trans-[CH]<sub>x</sub> with a reducing agent such as liquid sodium amalgam or sodium naphthalide (Salaneck, 1993).



The antibonding  $\pi^*$  system is partially populated and induces an increase in conductivity to  $10^3 \text{ Scm}^{-1}$ .

The electrochemical cathodic reduction can also induce the n-doping by immersing a trans-[CH]<sub>x</sub> film in a solution of LiClO<sub>4</sub> dissolved in THF, and attaching it to the negative terminal of a DC power source, while the positive terminal is attached to an electrode immersed in the solution, via



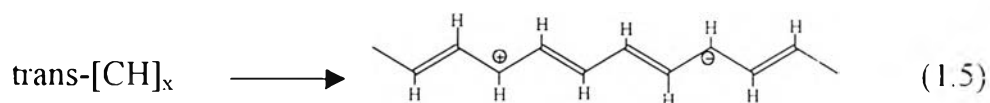
Both chemical and electrochemical p- and n- doping processes can dope not only [CH]<sub>x</sub>, but also other conductive polymers as well. Counter

"dopant" ions will stabilize the charges on the polymer backbone. In each case, spectroscopic signatures of polaron and bipolaron are obtained. However, there are still the other doping processes in which no counter ion is involved.

## 2. Redox doping involving no dopant ions

### *-Photodoping*

This type of doping can be done by exposing the polymer such as trans-[CH]<sub>x</sub> to the mediation of energy greater than its band gap, so the electrons are promoted across the gap and the polymer undergoes "photodoping"



The negative and positive charges present in the chain can delocalize along the polymer chain and photoconductivity is observed. These charges will disappear due to the recombination of electrons and holes when irradiation is discontinued.

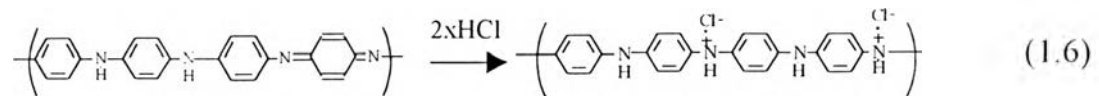
### *-Charge-Injection doping*

This doping type uses a metal/insulator/semiconductor (MIS) configuration; metal and conductive polymer are separated by a thin layer of a high dielectric strength insulator. A potential is applied across the structure to create a surface charge layer or the "accumulation" layer, which has been extensively investigated for conductive polymers (Salaneck, 1993). The resulting charges are present in the polymer without associated dopant ions.

## 3. Non-redox doping

In contrast to redox doping, in this doping type the number of electrons associated with the polymer backbone does not change. The first example of the doping of an organic polymer is the emeraldine base form of polyaniline. This can be accomplished by treating emeraldine base with an

aqueous protonic acid which results in an increase in conductivity by about nine to ten order of magnitude (up to  $10^2 \text{ Scm}^{-1}$ ) and produces the protonated emeraldine base (Genies, 1985).



After doping, the doped conjugated polymer or conductive polymer shows good electrical conductivity for 2 reasons:

1. Doping leads to injection of carriers into  $\pi$  electron system
2. The  $\pi$ -bonding leads to  $\pi$  electron delocalization along the polymer chain and, thereby, to the possibility of charge carrier mobility

### 1.1.3 Charge Carriers and Electrical Conductivity in Conductive Polymers

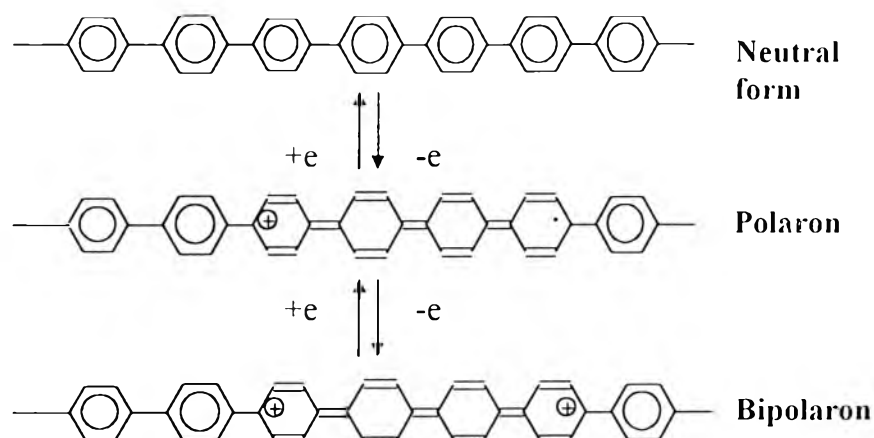
The electrical conductivity of conductive polymers depends on many parameters: the density of mobile charges or the number of carriers per unit volume ( $n$ ), the electronic charge ( $e$ ) and the carrier mobility ( $\mu$ ). The relationship between an electrical conductivity ( $\sigma$ ) and those parameters is expressed via the general equation (Smith, 1974)

$$\sigma = ne\mu \quad (1.7)$$

The band theory is usually used to explain electrical conductivity in the solid state. It is assumed that a solid consists of  $N$  atoms which are tightly packed together, and each individual electronic energy states split into  $N$  levels. Because the energy levels are spaced closely, the discreteness of the levels may be ignored and can be considered as a continuous energy band. The highest occupied energy is defined as the valence

band and the lowest unoccupied energy band is defined as the conduction band. After applying the electric field, the charge carriers with an energy near the top of the valence band can contribute to the conduction band which is empty (Chance, 1984). The ease of electron mobility across the band gap is dependent on the magnitude of the band gap and the width of band gap ( $E_g$ ).

The charge carriers in conductive polymers are different from those of metal (Chance, 1984); metals have unpaired electrons and there are no forbidden gap. When the temperature increases, the conductivity decreases due to lattice defects in the lattice and vibrational distortions (usually called “phonons”). Phonon activity increases with elevated temperature. For conductive polymers, the electrons are paired. The energy difference between the conduction band and the valence band gives rise to the intrinsic insulating or semiconducting properties of conjugated organic polymers. The electrical conductivity of these materials is promoted by thermal excitation of electrons from the valence band to the conduction band, so the electrical conductivity will increase with temperature in the neutral or undoped state. Lattice distortions can occur when one electron is removed or added into the polymer chain forming a radical cation or radical anion, respectively (James, 1980). The lattice distortion leads to an upward shift of electrons from the valence band to the conduction band and downward shift from the conduction band to the valence band. The radical ion associated with a lattice distortion is called “polaron” and when the second electron is removed from or added to this polymer, the dication or dianion, usually called “bipolaron”, is formed. At higher doping levels, the bipolaron will interact and form a polaron band within the energy gap as illustrated in Figure 1.3:

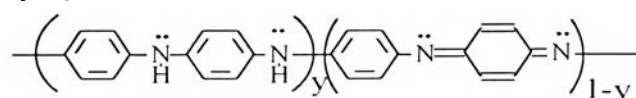


**Figure 1.3** The polaron and bipolaron defects in poly (p-phenylene).

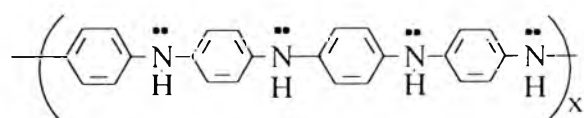
## 1.2 Polyaniline

Polyaniline constitutes an important class of conductive polymer and can be formed by chemical and electrochemical oxidative polymerizations of aniline or its ring- or N-substituted derivatives in aqueous acid solution (Salaneck, 1980; Huang, 1986).

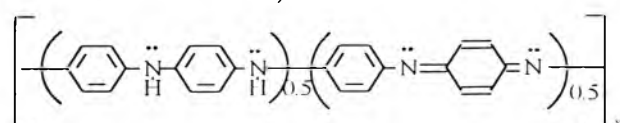
The base form of polyaniline has the generalized structure:



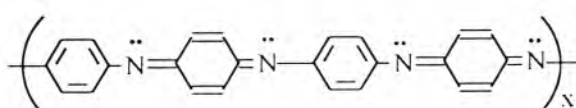
which consists of alternating reduced,  $\left( \text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-NH} \right)$ , and oxidized,  $\left( \text{C}_6\text{H}_4\text{-N}=\text{C}_6\text{H}_4\text{=N} \right)$  repeat units (Kang, 1998). The average oxidation state, (1-y), can be varied from a) 0 to give the completely reduced form



b) 0.5 to give the half oxidized form,



and c) 1 to give the completely oxidized form,



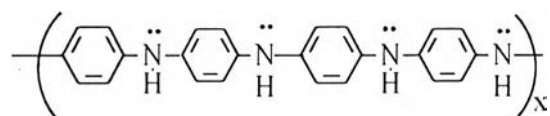


Polyaniline of  $(1-y) = 0, 0.5$  and  $1$  are called leucoemeraldine, emeraldine and pernigraniline, respectively. Some base forms of polyaniline can be rendered into a conductive form (emeraldine salt) by chemical or electrochemical doping processes, leading to an increase in electronic conductivity of about ten orders of magnitude (MacDiarmid and Epstein, 1989).

### 1.2.1 Electronic Structure of Polyaniline Base Forms

#### 1. *Leucoemeraldine Base*

This form of polyaniline corresponds to the fully reduced form in which all nitrogen atoms are amine (-NH-). The leucoemeraldine base can be called poly(p-phenylene amine) (Salaneck, 1993).

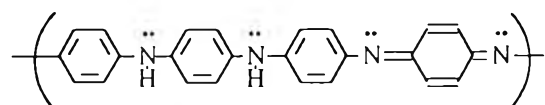


In the leucoemeraldine base, all nitrogen atoms define a single plane which is also common to all nitrogen-carbon and nitrogen-hydrogen bonds; there is, therefore, effective  $sp^2$  hybridization of nitrogen and each lone pair on nitrogen atoms effectively carries two  $\pi$  electrons. In terms of molecular orbital, the upper  $\pi$  band is fully occupied because there is an even number of  $\pi$  electrons which is equal to 8 per ring-nitrogen unit,  $\left( \text{C}_6\text{H}_4\text{NH} \right)_x$ , giving this polyaniline base form a very large band gap of about 3.8 eV (Salaneck, 1993). One of the most peculiar characteristics of the electronic structure of leucoemeraldine base is the lack of electron-hole symmetry, i.e. the upper occupied band and the lower unoccupied band have widely different wave function characteristics. The wave function characteristic of the upper occupied band is reminiscent of one of the degenerate HOMO (Highest Occupied Molecular Orbital) levels of benzene. The lower unoccupied band wave function corresponds to that of one benzene LUMO (Lowest

Unoccupied Molecular Orbital) level, that is fully localized within the ring. As a result, there is no significant wave function interaction from ring to ring and that band acquires no dispersion leading to the insulating property. That means the leucoemeraldine base is an insulator (Salaneck, 1993).

### 2. Emeraldine Base

The emeraldine base form is called the half-oxidized form because the number of amine nitrogen atoms (-NH-) is equal to the number of imine (-N-) nitrogen atoms. Thus, emeraldine base corresponds to poly(p-phenylene amine-imine) (Salaneck *et al.*, 1980). Along the chain of emeraldine base, two amine nitrogen atoms are followed by two imine nitrogens. Because of the chemical oxidation of leucoemeraldine base, there are two  $\pi$  electrons less than in the leucoemeraldine base per four ring-nitrogen unit.



The imine nitrogen indeed contributes a single  $\pi$  electron, its lone pair now lying within the molecular plane. The band gap in emeraldine base is of the order of 1.4 eV (Salaneck, 1993). It is due to the loss of glide-plane symmetry because of the presence of a ring with quinoid geometry between two amine nitrogen atoms. The destabilization on quinoid ring between imine nitrogen makes the emeraldine base show a semiconducting property.

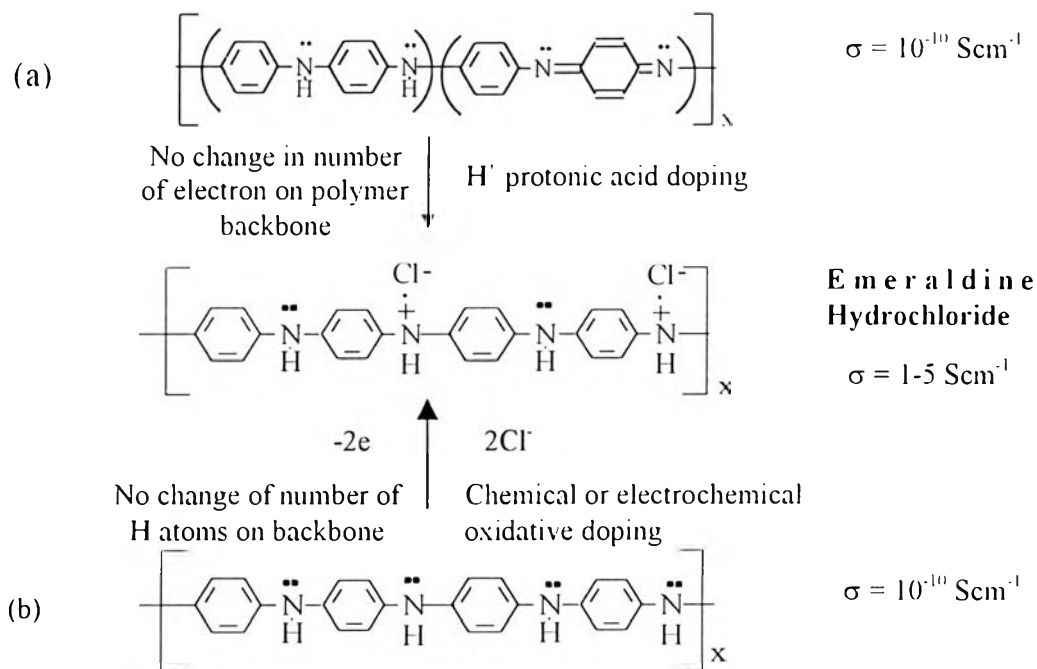
### 3. Pernigraniline Base

Pernigraniline base is the fully oxidized form of polyaniline since all nitrogen atoms are imine (-N-) nitrogen atoms, thus pernigraniline base corresponds to poly(p-phenylene imine) (Salaneck, 1993). The translational unit contains two ring-nitrogen unit  $\left( \text{C}_6\text{H}_4\text{=N-C}_6\text{H}_4\text{=N} \right)$ . This form of polyaniline has no glide-plane symmetry as in the case of emeraldine base, the ring alternates between an aromatic geometry and a

quinoid geometry. Each ring-nitrogen unit carries an odd number which is equal to 7  $\pi$ -electrons. Therefore, if the glide plane symmetry is retained along the chain, we would be dealing with a half-filled band system. However, the structure of pernigraniline is unstable with respect to a symmetry breaking leading to the opening of a Piers gap and a semiconducting state. The band gap of pernigraniline base is 1.8 eV (Salaneck, 1993).

### 1.2.2 Doping of Polyaniline

Polyaniline holds a special position amongst conductive polymers in that its most highly conducting doped form can be reached by two completely different processes; protonic acid doping of emeraldine base and oxidative doping of leucoemeraldine base (James, 1980) as shown below:

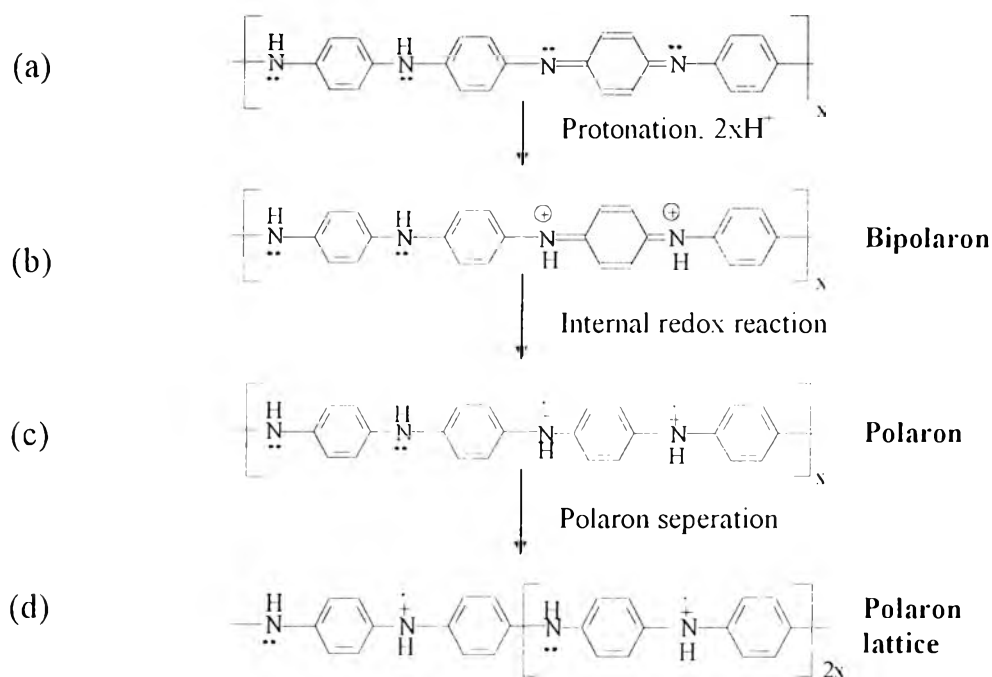


**Figure 1.4** The schematic representations of emeraldine hydrochloride formation by (a) protonic acid doping of emeraldine base and (b) oxidative doping of leucoemeraldine base.

In terms of protonic acid doping of the emeraldine base, the doping process uses a protonic acid as a dopant, for example, 1M aqueous HCl

resulting in a complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt (Genies, 1985).

The protonated polyaniline is actually a polysemiquinone radical cation (Salaneck, 1993; MacDiarmid and Epstein, 1989); one resonance form consists of two separated polarons resulting from an “internal” redox reaction. Then the polaron is separated to polaron lattice to minimize the electrostatic repulsion between positive charges (Salaneck, 1993). The oxidation states of all rings become equivalent, so the charges and spins are placed on the other sets of nitrogen atoms. The overall structures are expected to have extensive spins and charges delocalization resulting in a half-filled polaron conduction band and an increase in the electrical conductivity by over ten orders of magnitude without any changes in the number of electrons on the polyaniline backbone (Genies, 1985; MacDiarmid and Epstein, 1989).



**Figure 1.5** The sketch of the geometric structures evolution of emeraldine base as a function of protonation (a) before protonation, (b) formation of bipolaron, (c) dissociation of bipolaron into polaron and (d) formation of a polaron lattice.