

CHAPTER II

THEORY

2.1 Polyaniline

2.1.1 Properties of Polyaniline

PAni is one of the conductive polymers synthesized by chemical oxidation or electrochemical polymerization in the presence of acid media. PAni has a general formula shown in Figure 2.1 containing reduced repeating units, and oxidized repeating units.

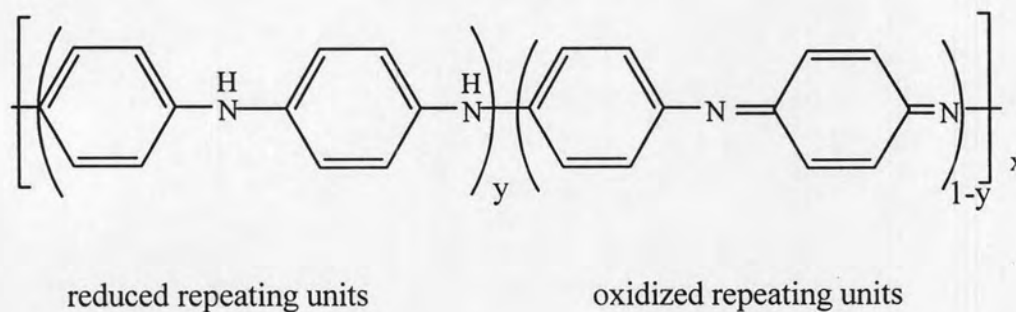


Figure 2.1 General formula of PAni.

Table 2.1 summarizes the property of conductivity of PAni depending on its form, according to y -value. The conductive form of PAni is the protonated polyemeraldine or polyemeraldine salt (PAni-ES) whose color is green and the conductivity is around 15 Scm^{-1} [56]. Conductivity of polyemeraldine base (PAni-EB) is around 10^{-5} Scm^{-1} . Note that the conductivity of a metal is around 10^3 Scm^{-1} .

Table 2.1 The different forms of PANi.

y-value	Name	Color	Conductivity (Scm ⁻¹)	Structure
1 (reduced form)	Leucoemeraldine base (PANi-LEB)	Yellow	<10 ⁻⁵	
0.5	Emeraldine base (PANi-EB)	Blue	<10 ⁻⁵	
0 (oxidized form)	Pernigraniline base (PANi-PNB)	Purple	<10 ⁻⁵	
	Emeraldine salt (PANi-ES)	Green	~15	

Each oxidation state can exist in the form of its base or its protonated form (salt) by treatment with an acid. The different oxidation states of PANi can interconvert between each other under appropriate conditions. For example, the insulating PANi-EB form of PANi can be converted to the conducting PANi-ES formed by doping methods.

2.1.2 Polyaniline Synthesis

PAni is mostly synthesized by aniline oxidation either with a chemical oxidant (chemical route) or through electrochemistry. Other synthesis are also proposed for example, plasma polymerization [57], autocatalytic polymerization [58] or inverse emulsion polymerization [59].

2.1.2.1 Chemical Synthesis

Chemical synthesis PANi requires three reactants: aniline, an acidic medium (aqueous or organic) and an oxidant. The common used acids are essentially hydrochloric acid (HCl) and sulfuric acid (H₂SO₄). Ammonium persulfate ((NH₄)₂S₂O₈), potassium dichromate (K₂Cr₂O₇), cerium sulfate (Ce(SO₄)₂), sodium vanadate (NaVO₃), potassium ferricyanide (K₃(Fe(CN)₆), potassium iodate (KIO₃) and hydrogen peroxide (H₂O₂) are recommended as oxidants [60, 61]. However, the most popular synthesis pathway is under 1 M aqueous hydrochloric acid solution (pH between 0 and 2) and using ammonium persulfate as oxidant with an oxidant/aniline molar ratio less than 1.15 in order to obtain high conductivity and yield [60]. The monomer concentration varies from 0.01 to 1 M. The polymerization is performed under 0 to 2 °C in order to limit secondary reactions. The duration of the reaction varies generally between 1 and 2 hours. The obtained material is polyemeraldine salt (PANi-ES): polyemeraldine hydrochloride (PANi-HCl), green colored. To obtain polyemeraldine base, polyemeraldine hydrochloride is treated in an aqueous ammonium hydroxide solution for 15 hours. The obtained powder is washed and dried as described earlier.

2.1.2.2 Electrochemical Synthesis

Three electrochemical methods can be used for PANi synthesis

- galvanostatic method, which a constant current is applied.
- potentiostatic method with a constant potential.
- potentiodynamic method, which current and potential are varied with time.

Whatever the method is, a three-electrode assembly composes in the reactor vessel: a working electrode on which the polymer is deposited, a counter electrode also named auxiliary electrode (platinum grid) and a reference electrode (in most cases, a saturated calomel electrode (SCE)). The more common working electrode is a platinum one, but PANi depositions have also been realized onto conducting glass (glass covered by indium-doped tin oxide (ITO) electrode), Fe, Cu, Au, graphite, stainless steel, etc [60]. PANi can be then peeled off from the electrode surface by immersion in an acidic solution. Compared to chemical synthesis, this route presents several advantages [62] such as cleanliness because no extraction from the monomer solvent-oxidant mixture is necessary, doping and thickness can be controlled via electrode potential, synthesis and deposition of PANi thin layer can be simultaneously occurs.

2.1.3 The Reason for Conduction in Polyaniline

The conducting of polymer can be explained by the molecular orbital theory. One carbon atom has six electrons, of which four can be used to create bonds to other atoms. One sp^2 orbital forms a bond with the hydrogen atom overlapping with its 1s orbital and other two forms σ -bonds with adjacent carbon atoms along the chain (overlapping the sp^2 orbitals). In forming the sp^2 orbital, one 2p orbital on carbon has not been used. The remaining p orbital (p_z) is oriented perpendicular to the plane of sp^2 orbitals. Along the polymer chain the p_z orbitals of two adjacent carbon atoms can overlap and form a π -bond. The π -bonds have smaller binding energy than σ -bonds. That is the reason why electrons will move more easily, called delocalization. This system of interacting p_z -orbitals is called the conjugated π -system and is the reason

for the unique electronic and optical properties of conjugated polymer. Extended overlap of the π -orbitals, intrinsic to conducting polymers, develops broad valence and conduction bands. The valence and conduction bands can be classified as π and π^* orbital bands, respectively [63]. All conducting polymers (and most of their derivatives), for example, polyacetylene, poly(p-phenylene), polythiophene, polypyrrole, polyaniline and etc. (Figure 2.2). The conductive properties of these polymers arise from the doping process. Doping process of a polymer can be carried out by electrochemically or by exposing the polymer to a vapor or a solution consisting of a dopant. There are two different routes in the doping processes; a dopant accepting charges (p-type) or donating charges (n-type) onto the polymer backbone. Because of the unique properties of conducting polymers, they are used in a wide range of applications. In the past, conducting polymers have been proposed for uses as conducting wires, in batteries, light emitting diode, as electromagnetic interference shielding materials, sensor, and etc.

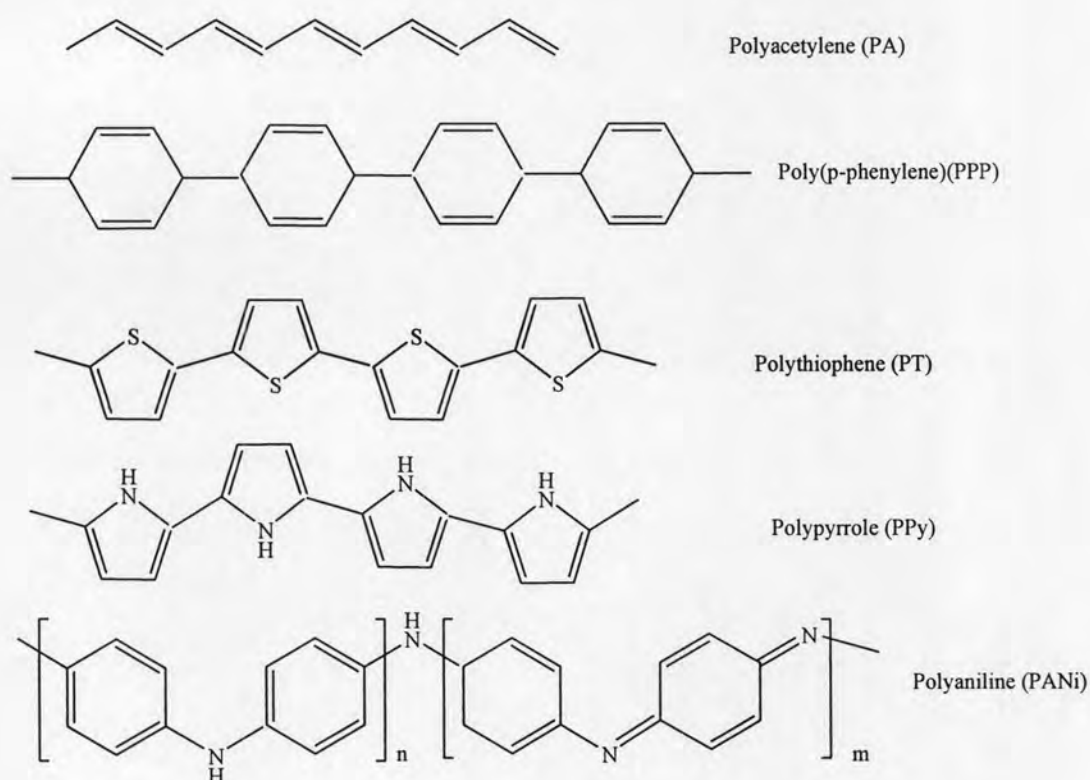


Figure 2.2 Structure for the most common conducting polymer.

2.1.4 Polyaniline 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 a p-type or an 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 sketched in Figure 2.3

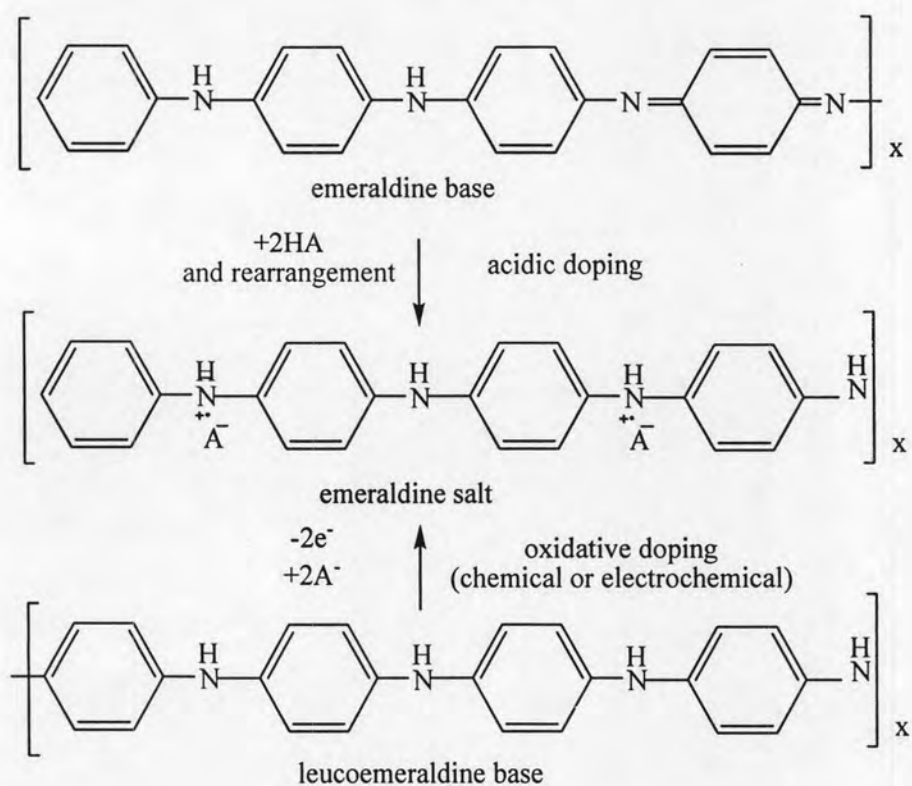
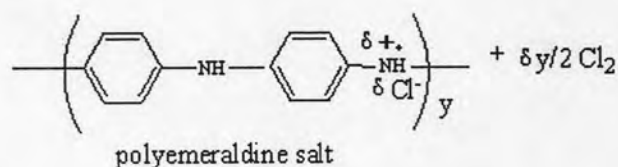
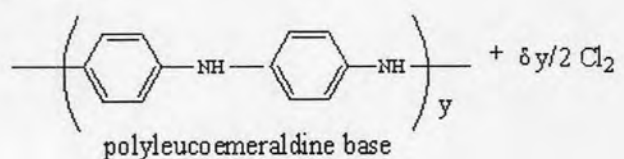


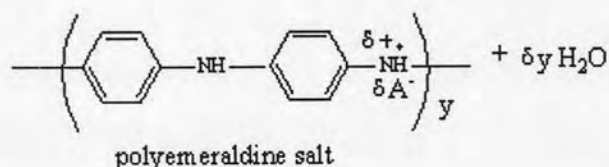
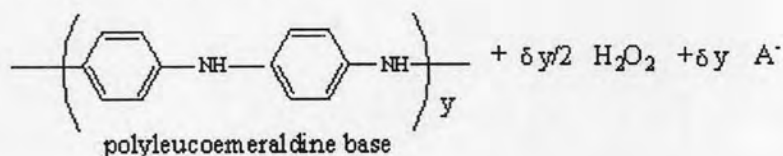
Figure 2.3 Doping mechanisms of PANi.

2.1.4.1 Oxidative Doping

The oxidative doping is known through chemical or electrochemical processes from the totally reduced form of PANi: polyleucoemeraldine base. Polyleucoemeraldine base is prepared by reduction of PANi-ES with phenylhydrazine or hydrazine solutions by dipping for 5 or 6 min [64]. The chemical oxidative doping is run either with a chlorine or a less toxic iodine agents in a carbontetrachloride solution, or with $(\text{NO})^+(\text{PO}_6)^-$, FeCl_3 or SnCl_4 organic solution, or with oxygen or hydrogen peroxide in an aqueous acidic solution. The following examples illustrate the oxidative doping with Cl_2 :

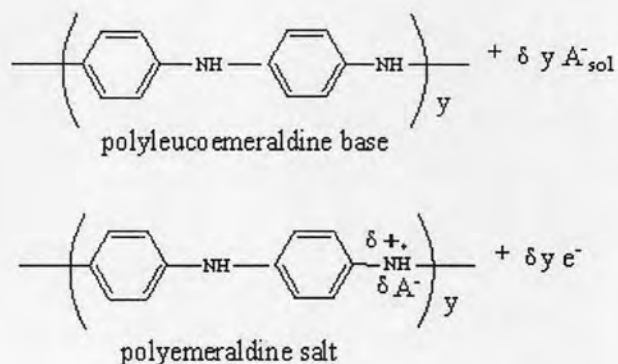


And with H_2O_2 in an acidic solution HA:



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 efficient process, 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 [65]. The electrochemical doping of polyleucoemeraldine base can be written as:



The counter-ion A⁻ of the electrolytic solution is inserted in the polymer backbone.

2.1.4.2 Acidic Doping

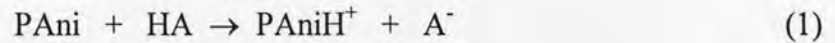
The acidic doping is a rare doping case where no change of the number of electrons associated with the polymer backbone occurs. The acidic doping consists to treat the PANi-EB with a strong acid (HCl, H₂SO₄) that induces the protonation of the imine sites to give the PANi-ES, through a mechanism illustrated in Figure 2.3. Considering the resonant structures, charge and spin can be largely delocalized that explains the observed conductivity (cf. Table 1.1). However, drawbacks of hydrochloride PANi-ES are its poor solubility in most common solvents, and its conductivity alteration with moisture and temperature. Then to improve the solubility of conducting polymers and their temperature stability (up to 200°C), three approaches have been developed [45, 66-69].

One of them implies the use of dopants other than HCl in the monomer solution. So, polyacrylic acid [45] or other polymeric acids, acrylic acid (AA) [66], lithium salts [67] and voluminous acids, specially sulfonic acids with a long backbone as dodecylbenzensulfonic acid (DBSA) or camphorsulfonic acid (CSA) have been added as dopants in the monomer solution. Moon Gyu Han et al. [70] have studied the

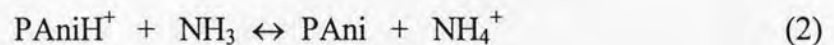
effects of DBSA and CSA dopants on thermal properties of PANi. Another approach to improve polyaniline solubility is the substitution of hydrogen atom from the aniline ring in ortho position with functional groups like CH₃, C₂H₅, OCH₃ and OC₂H₅ before the polymer synthesis. However, their conductivities are weak (10⁻¹ to 10⁻³ S cm⁻¹). Finally, the last approach is based on reaction between PANi-EB, once synthesized, with sulfuric acid [69]. This leads to the substitution of a hydrogen atom of the phenyl ring by a -SO₃H functional group, followed by the protonation of the imine groups to form a self-doped polymer.

2.2 Ammonia Sensing of Polyaniline

The mechanism of ammonia sensing depends on the type of dopant. As for the dopant, mineral acid HA (A⁻ = Cl⁻, HSO₄⁻, ClO₄⁻) are most often used. When the sensor is kept in an ammonia atmosphere, the layer resistance increases. The acid dissociates in solution into protons H⁺ and acid radical (A⁻), so the doping (protonation) reaction is of the form



Where PANi and PAH⁺ are the initial undoped repeated block and proton-doped repeated block of the PANi chains, respectively. As a result of such reaction, neutral PANi molecules gain protons, forming energetically favourable N⁺-H chemical bonds. So positively charged local centres placed at nitrogen atoms. Valence electrons can now hop from one such centre to another, giving rise to the p-type conduction. The current mechanism in this case may be treated as thermally activated hopping conduction [71]. When PANi is interacting with ammonia, the following reversible reaction occurs:



In the presence of ammonia this reaction goes predominantly towards the right: an ammonia molecule take up protons from PANi, thus forming energetically more

favorable ammonium, NH_4^+ . The last ions are held near negatively charged acid radicals (A^-). In fact, this is the PANi dedoping (deprotonation) reaction. But in the air (with no ammonia replenishment) the reaction (2) begins to go towards the left. Ammonium decomposes into ammonia (which volatilizes) and proton which, being added to PANi molecules, restore the initial level of doping. In such a way reversibility of the ammonia effect on PANi layers occurs, represented in Figure 2.4

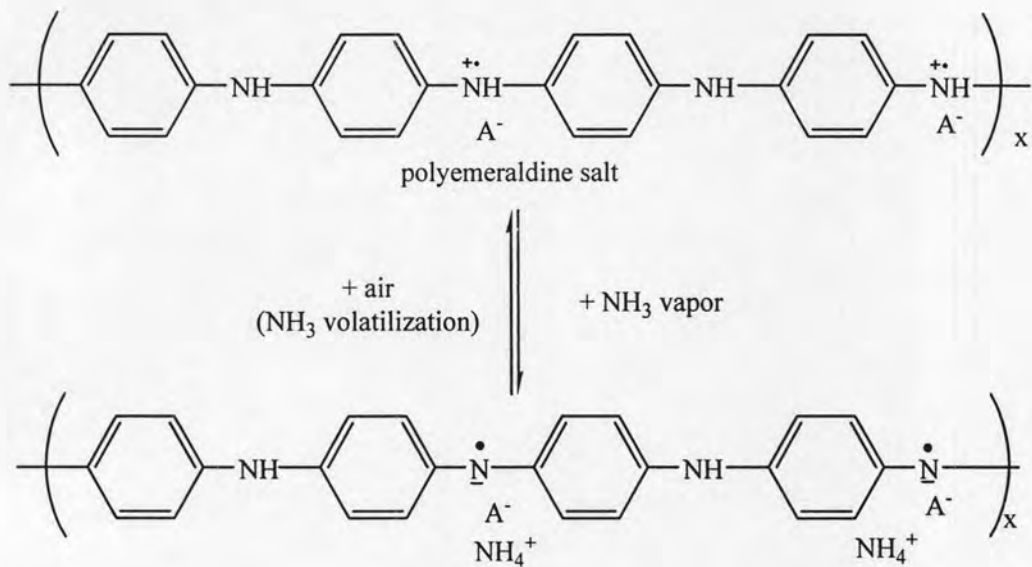


Figure 2.4 Interpretation of the sensitivity and reversibility of PANi-HA layer.

The deprotonation reaction causes the resistance of the PANi layer, R to grow. It was experimentally obtained that the resistance changes with the ammonia concentration, N , in following way:

$$R = R_0 \exp [(\alpha N)^\gamma] \quad (3)$$

Here R_0 is the initial resistance value (at a given temperature) for the PANi layer in air; α is a dimensional coefficient ($=5.65 \times 10^{-3} \text{ ppm}^{-1}$, if N is in ppm), and the parameter γ equals $\frac{1}{2}$. It should be noted that the expression (3) looks just like that for the resistivity ρ , f a disordered system : $\rho = \rho_0 \exp [f(N_D)]$, where $f(N_D)$ is an exponential function of impurity concentration N_D . (The last expression was derived

using the concept of percolation in disordered systems, and it describes the resistivity in the case of hopping conduction). The fact that in Equation (3) $\gamma = \frac{1}{2}$ suggests a two-dimensional character of the charge transfer in our PANi films, which the form of their resistance R dependence on the ammonia concentration N may serve as experimental evidence for the hopping conduction in these films.

Organic acids like acrylic acid [42] have also been used as dopants. Contrary to what is observed with mineral acids, the resistance of PANi-AA decreases when exposed to ammonia vapor, as explained in Figure 2.5 [42]. This behavior can be interpreted as follows. In ammonia atmosphere, NH_3 molecules in contact with PANi-AA can attack two types of adsorption sites $-\text{N}^+\text{H}-$ sites originated from HCl molecules present during polymerization reaction and acrylic acid molecules trapped in polymeric chains. As seen before, NH_3 adsorption onto $-\text{N}^+\text{H}-$ sites leads to an increase of resistance. On the contrary, NH_3 adsorption on acrylic acid molecules permits to create a conduction site, leading then to the decrease in the material resistance. The last phenomenon predominates and explains the global decrease in the material resistance. The above interpretation is supported by FTIR analysis [42].

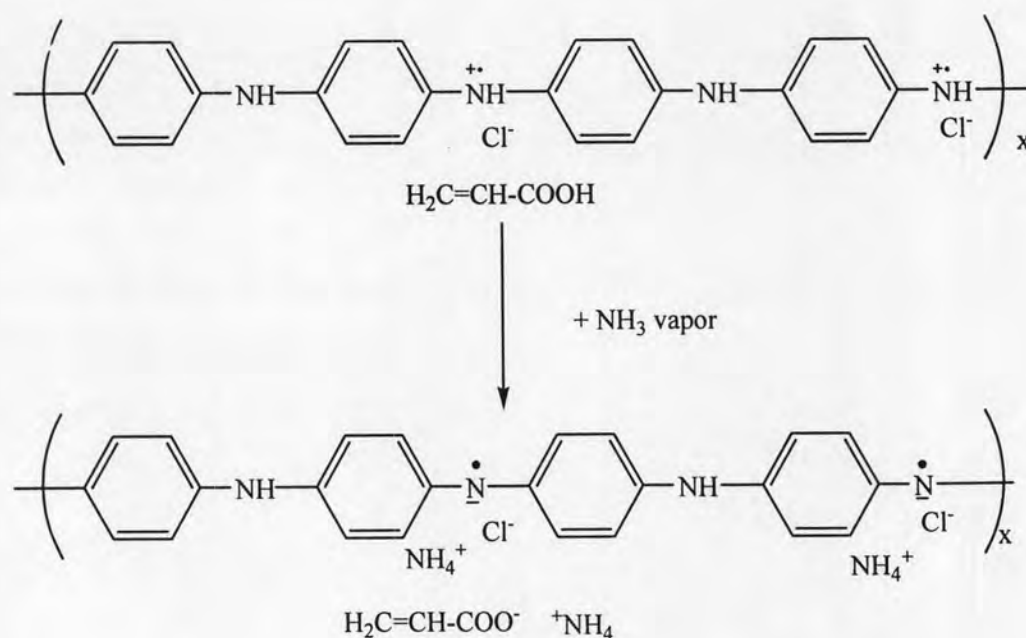


Figure 2.5 Interpretation of the sensitivity of PANi-AA sensor.

2.3 Polymer Blends

2.3.1 Process of Polymer Blending

Mechanical properties of polymer blends are very important in many applications. Significant for these properties are compatibility between the different polymers which is frequently defined as miscibility on a molecular scale of the components of the blend. Over 300 pairs of miscible polymers are known, from which only a few systems have been commercialised such as: Polyphenylether/Polystyrene (PPE/PS), Polycarbonate/Polyethylenterephthalate (PC/PET), and Polycarbonate/Polybutylterephthalate (PC/PBT). Another type of blend consists of incompatible polymers for which various morphologies can be realised via processing, for instance droplets or fibres in a matrix and stratified or continuous structures. The structures induced are usually unstable. For example addition of a rubber to a brittle polymer often creates an instable morphology, after processing this blend for the second time because the morphology may change. In most cases, melt mixing two polymers results in blends, which are weak and brittle. The incorporation of a dispersed phase into a matrix mostly leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases. Improving the mechanical properties of a blend is often done by modification which means modification of normally not miscible blends by mixing a block-copolymer into the blend to improve the miscibility. The end-use performance has been improved many times by this method. However this method is not the same as creating blends, which have miscibility on a molecular scale, or even blends containing very finely dispersed phases. From a practical point of view a blend often is considered to be compatible if a certain set of mechanical properties is achieved. Well known examples of blends are the impact modified, (rubber) toughened polymers, where polymers with different glass transition temperatures are blended. Many other blends are known such as barrier polymers for packing, where specific polar or apolar polymers are combined in order to increase the resistance against transport of water and gas (oxygen, carbon dioxide). It should be kept in mind that

several methods are known to improve the properties of plastics. For many polymers additives are needed to improve for example processability and lifetime (lubricants or stabilisers), modulus and strength (mineral fillers such as glass beads, chalk, clay, mica or glass-fibre reinforcement), appearance and colour (pigments), conductivity (conducting fillers such as aluminium flakes or carbon) or flammability (flame retardants). The word compatibiliser will sometime be replaced by alloying agent since a blend with improved mechanical properties is also called an alloy. Therefore this name can also be used since the improvement of the properties of the blend is the purpose of adding or creating a compatibiliser.

2.3.2 Properties of Polymer Blends

The incorporation of rubber particles within the matrix of brittle plastics may enormously improve their impact resistance. Toughening in brittle plastics is also observed under other loading conditions, such as simple low-rate stress-strain deformation and fatigue. When a force is applied to a blend several deformation mechanisms of the major phase and of cracks which are formed in the blend are important. Their relative importance may depend on the polymer and on the nature of the loading. The effect of the quantity of rubber incorporated and the method of forming the blend has been studied extensively for polystyrene/polybutadiene blends. An optimum rubber concentration and phase domain size exists, the values depending on the rubber and polymer concerned. The importance of grafttype bonding and the finer, more complex morphology developed in graft copolymers should be emphasised.

One prominent example is the microemulsion channel in ternary symmetric mixtures of A and B homopolymers, and AB diblock copolymers (see Figure 2.6).

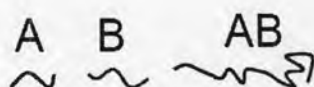


Figure 2.6 Schematic pictures of the components of a ternary A+B+AB polymer blend.