

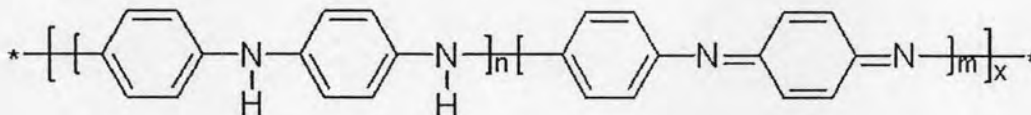
## CHAPTER II

### THEORY

#### 2.1 Polyaniline

##### 2.1.1 Properties of polyaniline

Polyaniline (PANi) is an organic conducting polymer. Polyaniline composes of aniline repeat units connected to form a backbone of alternating nitrogen atoms and benzene rings.



**Figure 2.1** General formula of PANi.

PANi exists in a variety of forms that differ in chemical and physical properties. It can classify into four groups depending upon the degree of oxidation of the nitrogen atoms: the leucoemeraldine base (LEB), the emeraldine base (EB) the pernigraniline base (PNB) and the emeraldine salt (ES). In Figure 2.1, x equals half the degree of polymerization. PANi-LEB with  $n = 1$ ,  $m = 0$  is the fully reduced state. PANi-PNB is the fully oxidized state ( $n = 0$ ,  $m = 1$ ) with imine links instead of amine links. PANi-EB is half oxidized state ( $n = 0.5$ ,  $m = 0.5$ ) form of polyaniline, often referred to as emeraldine base (EB), is either neutral or doped, with the imine nitrogens protonated by an acid into PANi-ES. PANi-EB is regarded as the most useful form of polyaniline due to its high stability at room temperature and the fact that upon doping PANi-ES is formed which electrically conducting. Leucoemeraldine and pernigraniline are poor conductors, even when doped with an acid.

**Table 2.1** The different forms of polyaniline.

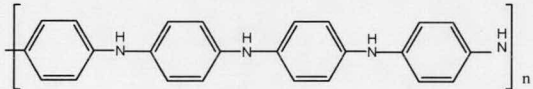
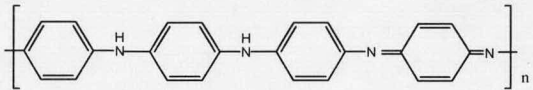
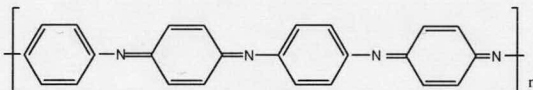
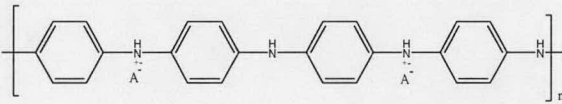
Form	Name	Color	Conductivity (Scm <sup>-1</sup> )	Structure
Reduced form	Leucoemeraldine base (PANi-LEB)	Yellow, White/clear	$< 10^{-5}$	
Half oxidized form	Emeraldine base (PANi-EB)	Blue	$< 10^{-5}$	
Oxidized form	Pernigraniline base (PANi-PNB).	Blue/Violet	$< 10^{-5}$	
	Emeraldine salt (PANi-ES)	Green	$\sim 15$	

Table 2.1 summarizes the property of conductivity of PANi depending on its form. The conductive form of PANi is the protonated polyemeraldine or polyemeraldine salt (PANi-ES) whose color is green and the conductivity is around  $15 \text{ Scm}^{-1}$  [30]. Conductivity of polyemeraldine base (PANi-EB) is around  $10^{-5} \text{ Scm}^{-1}$ . Note that the conductivity of a metal is around  $10^3 \text{ Scm}^{-1}$ . The color change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices. Though color is useful, the best method for making a polyaniline sensor is arguably to take advantage of the dramatic conductivity changes between the different oxidation states or doping levels [31].

## 2.1.2 Polyaniline Synthesis

Polyaniline can be synthesized by chemical oxidative and electrochemical polymerization.

### 2.1.2.1 Chemical synthesis

Chemical synthesis of polyaniline (PANi) is one of the most common methods of its production [32]. Aniline, an acidic medium (aqueous or organic) and an oxidant were used as the material for this synthesis. The most common synthesis of polyaniline is by oxidative polymerization with ammonium peroxydisulfate as an oxidant. The components are both dissolved in 1 M hydrochloric acid (proton acid is necessary to ensure producing a linear structured polymer product) and slowly (the reaction is very exothermic) added to each other with an oxidant/aniline molar ratio less than 1.15 in order to obtain high conductivity and yield [33]. However, the rate of polymer yield (solid precipitation) and the intrinsic structure of the resulting polymer are highly dependent on the pH of polymerization of the reaction medium [34]. 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 polymer precipitates as small particles and the reaction product is a dispersions. The obtained precipitate is polyemeraldine salt (PANi-ES):

polyemeraldine hydrochloride (PANi-HCl), green colored. Polyemeraldine hydrochloride is treated in an aqueous ammonium hydroxide solution for 15 hours which resulted in the formation of polyemeraldine base. The obtained powder is washed and dried.

### 2.1.2.2 Electrochemical synthesis

Electrochemical synthesis of polyaniline (PANI) is one of the most widely spread methods of its production without adding mixtures of an oxidant. For electrochemical synthesis, several methods can be used: galvanostatic, potentiostatic which a constant current is applied, cyclic voltammetry and other potentiodynamic methods which current and potential are varied with time. For all these techniques, a three-electrode system is the best choice to realize synthesis. This system composes of a working electrode which the polymer is deposited, a counter electrode (platinum grid) and a reference electrode (in most cases, a saturated calomel electrode (SCE)). Working electrodes made of various materials have been successfully applied in depositing conducting polymers, such as platinum, stainless steel, gold [3]. For 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 [34]. After that PANi can be peeled off from the electrode surface by immersion in an acidic solution. Compared to chemical synthesis, this route presents several advantages [35] 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.

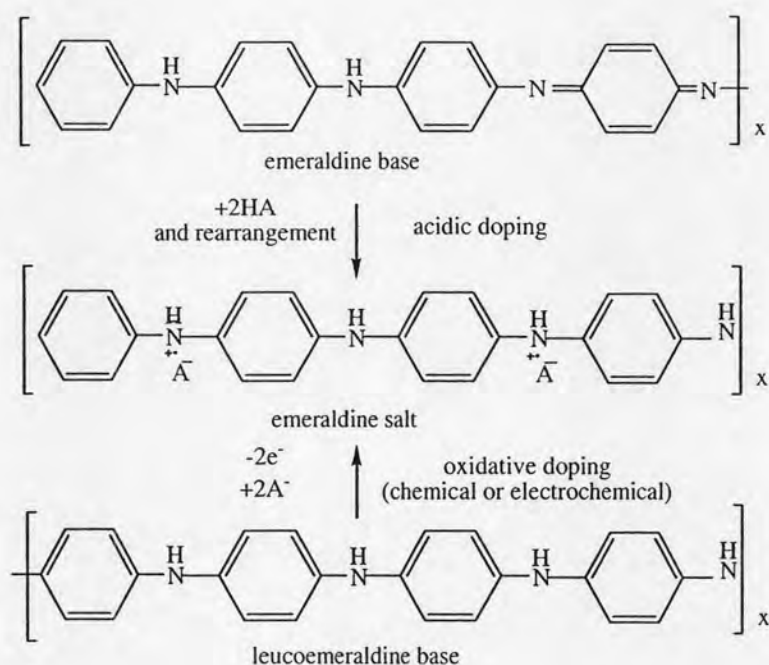
### 2.1.3 Polyaniline doping

The main chains of conducting polymer consist of alternative single and double bonds, which leads to broad  $\pi$ -electron conjugation. Conducting conjugated polymers offer major advantages in the facility with which the recognition elements can be tailored by chemical synthesis and thin film fabrication techniques. The incorporation of the conjugation along the backbone is of foremost importance

because it provides a pathway for electrons to migrate along a polymer chain and jump from one chain to another chain. To convert an insulating polymer to a conducting polymer, charge transfer agents, dopants are often require to inject electrons into delocalized framework or to remove electrons and leave positive holes. However, the conductivity of these pure conducting polymers are rather low ( $<10^{-5}$  S  $\text{cm}^{-1}$ ). In order to achieve highly conductive polymers, doping process is necessary. Conducting polymers can be doped by redox reaction or protonation.

Doping and undoping play key roles in the sensing mechanism of conducting polymer based sensors. The fundamental process of doping is a charge-transfer reaction between an organic polymer and a dopant. Conducting polymer doping consists to insert into the polymer, electron acceptor molecules (dopant accepting charges) or electron donor molecules (dopant donating charges). The obtained polymer is then a p-type or an n-type one, respectively. When charges are removed from (or added to) a polymer upon chemical doping, geometric parameters, such as bond length and angles, change. The charge is localized over the region of several repeating units. Since the localized charges can move along the polymer chain, they are regarded as charge carriers in conducting polymer. These quasi-particles are classified into polarons, bipolarons and solitons according to their charge and spin [36]. 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 2.2.





**Figure 2.2** Doping mechanisms of PANi.

### 2.1.3.1 Acidic doping

Type of doping mechanism is due to the presence of an  $\text{-NH}$  group in the polymer backbone, the protonation/deprotonation of which brings about a change in the electronic conductivity as well as in color [37]. It is well known that to impart conduction to PANi, doping it with an HA-type acid. The acidic doping consists to treat the PANi-EB with an HA type acid (such as HCl,  $\text{H}_2\text{SO}_4$ ) that induces the protonation to give the PANi-ES, through a mechanism illustrated in Figure 2.2. The acid dissociates in solution into proton  $\text{H}^+$  and acid radicals  $\text{A}^-$ . As a result of doping reaction, neutral PANi molecules gain protons forming energetically favorable  $\text{N}^+\text{-H}$  chemical bonds. Hence, the positively charged centers located at nitrogen atom are formed and valence electrons can hop from one such center to another, giving rise to conduction [8]. The acidic doping is doping where no change of the number of electrons associated with the polymer backbone occurs. Considering the resonant structures, charge and spin can be largely delocalized that explains the observed conductivity. Regarding the mechanism of electrical conduction Wan and Yang [38] reported that the overall conduction occurs both across and along the chain. The

former is dependant on the extent of  $\pi$  electron conjugation along the chain while the latter is dependant on the transport of charge carriers across the inter chain. At room temperature the principal way to increase the conductivity of the polymer is by enhancing the transport speed of the charge carriers, i.e., the mobility along the polymer chain and this depends on the conjugation length of the polymer at a given doping level. However, drawbacks of hydrochloride PANi-ES are its poor solubility in most common solvents, and its conductivity alteration with moisture and temperature. Therefore, to improve the solubility of conducting polymers and their temperature stability, polyacrylic acid [39] or other polymeric acids, acrylic acid (AA) [40], lithium salts [39] 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. [41]. In other words, dopants can influence the physical and chemical properties of conducting polymers. Conducting polymers doped with different ions may give distinct responses to a specific analyte.

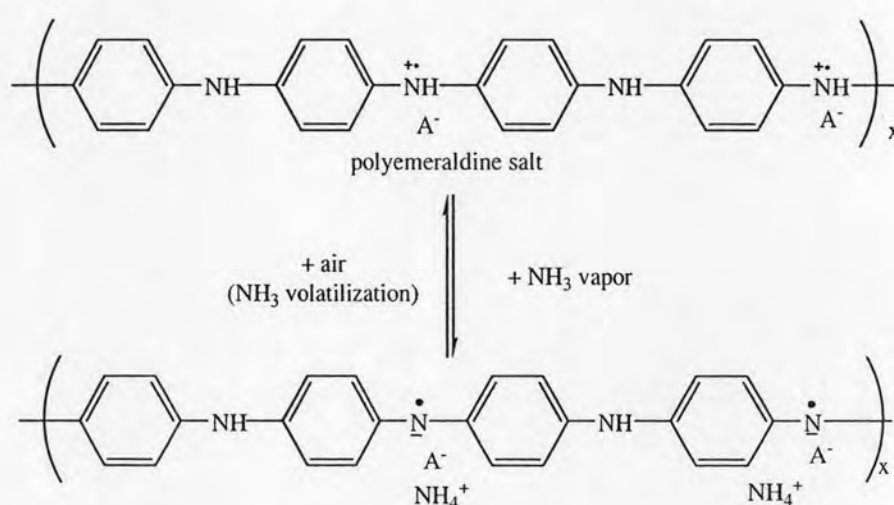
## 2.2 Ammonia sensing of polyaniline

Conducting polymer gas sensor common rely on conductivity changes that occur when they are exposed to certain gas. For the mechanism of ammonia sensing depends on the type of dopant, which mineral acid HA ( $A = Cl^-, HSO_4^-, ClO_4^-$ ) are most often used. When the  $NH_3$  molecules reach to the surface of the PANi, emeraldine salt (ES), they approach to the NH groups of the ES, interact with them and take proton from them to form the energetically more favorable  $NH_4^+$ . So the ES state has been reduced to the emeraldine base state (EB), resulting in significant changes in electrical resistance, increase of electrical resistance. This reaction is the PANi dedoping (deprotonation). In the air (with no ammonia replenishment), ammonium decomposes into ammonia (which volatilizes) and proton which, being added to the EB state of PANi, and restore the initial level of doping, ES. This gives the effect of reversibility of adsorption of ammonia on PANi surface, represented in Figure 2.3. The electrical resistance change is reversible, indicating that it is possible to use a PANi as ammonia gas sensing material. The resistance change of a PANi is

controlled by ammonia diffusion into the PANi, which can be expressed by the following equation [8]:

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

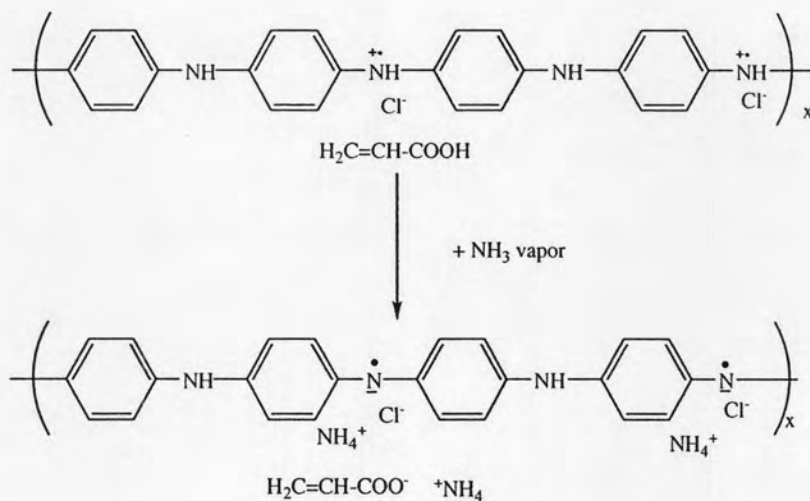
Here,  $R_0$  is the initial resistance,  $N$  the ammonia concentration where  $\alpha$  and  $\gamma$  are constants.



**Figure 2.3** Interpretation of the sensitivity and reversibility of PANi-HA layer.

Acrylic acid (AA) have also been used as dopants. The resistance of acrylic acid doped PANi is decreased when exposed to ammonia vapors, as explained in Figure 2.4 [12]. In comparison with conventional PANi, acrylic acid doped PANi exhibited an inverse response. This behavior can be interpreted by considering the interaction of  $NH_3$  with the dopant AA. In the ammonia vapor,  $NH_3$  molecules can attack with PANi-AA two adsorption sites:  $-N^+H-$  sites originated from HCl molecules present during polymerization reaction and acrylic acid molecules trapped in polymeric chains. As seen before,  $NH_3$  adsorption onto  $-N^+H-$  sites leads to an increase of resistance. On the contrary,  $NH_3$  molecule may take up a hydrogen from AA forming  $NH_4^+$  which creates  $-COO^-$  anion in the polymer chain and leaving a conduction site, leading then to the decrease in the material resistance [14].





**Figure 2.4** Interpretation of the sensitivity of PANi-AA sensor.

### 2.3 Fabrication of polymer sensor

Active layer is the heart of a sensor. Various techniques have been developed to prepare conducting polymer films, in order to adapt to different sensing materials and different types of sensor configurations. Different methods exist to deposit PANi onto a substrate, i.e., casting, spin-coating, electrochemical deposition, dip-coating, drop-coating, electrospinning, thermal evaporation, Langmuir-Blodgett (LB), selfassembly techniques [3, 42]. Polymeric nanofiber is also fabricated as a gas sensor. A number of techniques are available such as drawing, template synthesis, phase separation and electrospinning.

## **2.3.1 Preparation of conducting polymer films**

### **2.3.1.1 Electrochemical deposition**

Electrochemical deposition is the most convenient method to deposit conducting polymer films. The thickness of the film can be controlled by the total charge passed through the electrochemical cell during film growing process. Moreover, the film can be deposited on patterned microelectrodes [43] and the deposition must be carried out on a conducting substrate. However, if the insulating gap between the neighboring electrodes is close enough (several tens of micrometer), the growing film can cover the insulated gap and connect electrodes [44]. This is important in fabricating chemiresistors. The drawback is that electropolymerization is restricted by the use of conducting substrate, no deposition can be obtained on insulating surface.

### **2.3.1.2 Dip-coating**

It is a chemical deposition by dipping the substrate into the polymerization solution. When dipping a substrate into a chemical polymerization solution, part of the polymer will be deposited spontaneously onto its surface, the other part precipitates in the solution [45, 46]. This process occurs on different substrates, and the thickness of the film is usually controlled by dipping time.

### **2.3.1.3 Drop coating**

A polymer solution is drop dried [47, 48], or some drops of the monomer and oxidant solutions are dropped and reacted on a substrate surface. This technology is rather simple. The advantage of this process is that polymerization occurs only at the surface so no polymerization in the solution is observed. However, the resulting film is usually not uniform.

#### **2.3.1.4 Spin-coating**

Spin-coating is a simple method for preparing films from soluble conducting polymers. In this process, the conducting polymer solution is spread on the rotating substrate [49, 50]. After evaporation of solvent, a thin film was formed, which can control the thickness of the film by repeating above process. Solution viscosity, rotating rate of the substrate and duration are also plays important roles in adjusting the thickness of the formed film. This method can coat conducting polymers on both conducting and insulating substrates.

Polyemeraldine salt being insoluble in most ordinary solvents, the general procedure consists to use polyemeraldine base dissolve in an adequate solvent (NMP). The solution is then deposited onto the substrate by spin-coating. The obtained polyemeraldine base film is then doped by dipping the modified substrate into an aqueous hydrochloric acid solution, in order to obtain a thin layer of polyemeraldine salt on the substrate surface [42].

#### **2.3.1.5 Casting**

Conventionally, a film casting process is used to produce thin membranes. The process operated by the polymer solution is poured into a glass substrare, and then allowed to solidify by evaporating of solvent. The solidified part is also known as a casting, which is ejected from the glass to complete the process. The thickness of the film can be controlled during casting process.

#### **2.3.1.6 Thermal evaporation**

Thermal evaporation deposition technique consists in heating until evaporation of the material to be deposited. The material vapor finally condenses in form of film on the cold substrate surface and on the vacuum chamber walls. Usually low pressures are used, about  $10^{-6}$  or  $10^{-5}$  Torr, to avoid reaction between the vapor and atmosphere. At these low pressures, the mean free path of vapor atom is the

same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. The thickness of the film is determined by the evaporation duration [51].

### **2.3.1.7 Langmuir-Blodgett (LB)**

LB technique is a famous method to produce a thin film of polymer and surfactant. The operation of LB technique has been described in many books and literatures. Two different ways are reported to deposit a conducting polymer film by LB technique: directly depositing polymer and depositing monomer followed by polymerization on the substrate. A LB film is ultrathin (monomolecular layer), each run corresponds to one monolayer and a thick film can be obtained by repeating the procedure of LB deposition. So, the advantage of this technique is the possibility to control the number of deposited layers [42].

### **2.3.1.8 Layer-by-layer (LBL) self-assembly techniques**

This technique consists to immerse alternatively the substrate into a polymeric anion solution and a polymeric cation solution, an alternative composite film (layer by layer) consists of the two polymeric electrolytes is fabricated [52, 53]. Doped conducting polymers such as PANi, bring positive charge on their backbone, which allow it possible to deposit with a polymeric anion. Repeating the process, a multilayered film is obtained. The thickness of the LBL film depends on the number of repeating times.

## **2.3.2 Preparation of polymeric nanofibers**

### **2.3.2.1 Drawing**

Nanofibers have been fabricated through the process of drawing. A micropipette with a diameter of a few micrometers was dipped into the contact line using a micromanipulator. The micropipette was then withdrawn from the

liquid and moved at a speed of approximately  $1 \times 10^4 \text{ ms}^{-1}$ , resulting in a nanofiber being pulled [54]. The pulled fiber was deposited on the surface by touching it with the end of the micropipette. The drawing of nanofibers was repeated several times on every droplet. The viscosity of the material at the edge of the droplet increased with evaporation and drawing a fiber requires a viscoelastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pulling. The advantage of drawing process was minimizing equipment required. However, process of drawing was discontinuous.

### **2.3.2.2 Template synthesis**

Template synthesis implies the use of a template or mold to obtain a desired material or structure. Creation of nanofiber, the template refers to a metal oxide membrane with through thickness pores of nano-scale diameter [54]. Under the application of water pressure on one side and restraint from the porous membrane causes extrusion of the polymer which, upon coming into contact with a solidifying solution, gives rise to nanofibers whose diameters are determined by the pores. Fibers of different diameters can be easily achieved by using different templates.

### **2.3.2.3 Phase separation**

In phase separation, a polymer is firstly mixed with a solvent before undergoing gelation. The main mechanism in this process is the separation of phases due to physical incompatibility. One of the phase - which is that of the solvent - is then extracted, leaving behind the other remaining phase, which consists of 5 major steps: (i) polymer dissolution, (ii) gelation, (iii) solvent extraction, (iv) freezing and (v) freeze-drying [54]. Process can directly fabricate a nanofiber matrix. Batch-to-batch consistency is achieved easily. Mechanical properties of the matrix can be tailored by adjusting polymer concentration and minimum equipment requirement. However, this process was limited to specific polymer.



### 2.3.2.4 Electrospinning

Electrospinning or electrostatic spinning is an interesting technique that employs electrostatic forces to produce polymer fibers, ranging in diameter from sub-micrometers down to nanometers. Due to the high surface area to volume ratio, high porosity, very small size, and light weight of the electrospun fibrous, they have a variety of applications such as tissue scaffolding, highly efficient filtration membranes, nanowires, nanocomposites and electrical and optical materials [21, 22]. The electrospinning process is the use of electrostatic force as the main driving force for fiber formation. In the process, a high voltage power supply is used to charge a polymer solution or melt through a metal contact, e.g. normally a needle, across a metal collection screen. The applied potential is in the range of 5 to 30 kV, depending on the collection distance. A reservoir containing a polymer solution or melt is attached to the metal contact with the small opening. When the polymer solution or melt is charged, the Coulombic repulsion force destabilizes the hemispherical pendant droplet located changes in to a conical shape, which normally terms "the Taylor's cone" Further increase in the applied potential causes a charged jet to be ejected from the tip of the Taylor's cone. At right condition, fiber is formed as a result.

## 2.4 Electrospinning process

In 1934, Formhals [54] was granted the first patent detailing an apparatus and a process for producing polymer fibers by using electrostatic force, the process is termed as electrospinning. In other words, electrospinning is a process that creates nanofibers through an electrically charged jet of polymer solution or polymer melt. The electrospinning process, in its simplest form consisted of polymer solutions or melts can be carried out either horizontally or vertically, depending on the direction of normal line between the tip of the needle and the collection screen, two electrodes and a DC voltage supply in the kV range. The reservoir can be anything from a pipette to a syringe. In the case of glass pipette, the high electric potentials were supplied in the solutions or the melts directly. On the other hand, when a syringe was used as the

reservoir, the high electric potentials can be applied directly to the solutions or melts through a metal needle by attaching with the metal electrode. Collection screens from a metal foil or sieve of different geometry have been used as targets to receive the charged jets.

The polymer is ejected from a needle with forms a continuous nanofiber when the electrical force (due to the high electric potential of the polymer solution) overcomes the surface tension. At this point the pendant droplet of the polymer solution at the tip of the needle is deformed into conical shape, typically referred to as Taylor cone. When the critical voltage is exceeded, the electrical force overcomes the surface tension and a fine charged jet is ejected. After the jet flows away from the droplet in a nearly straight line, it bends into a complex path and other changes in shape occur, during which electrical forces stretch and thin it by very large ratios. After the solvent gradually evaporates solid nanofibers are left to accumulate on the collection screen as shown in Figure 2.7.

#### **2.4.1 Pathway of nanofibers formation**

The mechanism for the fiber formation in the electrospinning process could be divided into different region. Reneker and Fong (2006) have separated the electrospinning process into several stages for convenience of description: launching of the jet; elongation of the straight segment; development of whipping instability; and solidification into a fiber. However, the first stage subdivided into droplet generation stage and a Taylor's cone formation stage.

##### **2.4.1.1 Droplet generation**

The charging of a droplet of polymer solution is the initial step in electrospinning. Typically, a polymer solution is pumped at a low flow rate into a needle tip. In the absence of an applied electric field or if the electric field is not too large, the droplets form at end of needle and fall off under the influence of gravity. Assuming the surface tension of the liquid,  $\gamma$ , and the gravitational force,  $F_G$ , to be the

only two forces acting on the meniscus of the droplet, the radius of the droplet,  $r_0$ , produced by the needle of internal radius  $R$  is

$$r_0 = (3R \gamma / 2 \rho g)^{1/3}$$

where  $\rho$  is the density of the liquid and  $g$  is the gravitational constant.

When the droplet are electrically charged by applying an high enough electric potential difference between the droplet and collector, the electric force  $F_E$ , as well as the gravitational force, will work against the needle surface force (i.e.,  $F_\gamma = F_E + F_G$ ) and the droplet size at the needle tip will be reduced to  $r$  ( $r < r_0$ ). For electrospinning process, where a needle carrying a positive voltage,  $V$ , is held at a distance,  $L$ , from a collector,  $F_E$  for the system can be expressed as in equation.

$$F_E = (4\epsilon\pi V^2) / [\ln(4L/R)^2]$$

where  $\epsilon$  is the permittivity of the medium (air in most experiments), and  $V$  is the applied electric potential. The droplet radius  $r$  for such a system can be expressed as in equation, produced by Bugarski et al.

$$r = \{(3/2\rho g)[R_\gamma - (2\epsilon V^2)/(\ln(4L/R))]\}^{1/3}$$

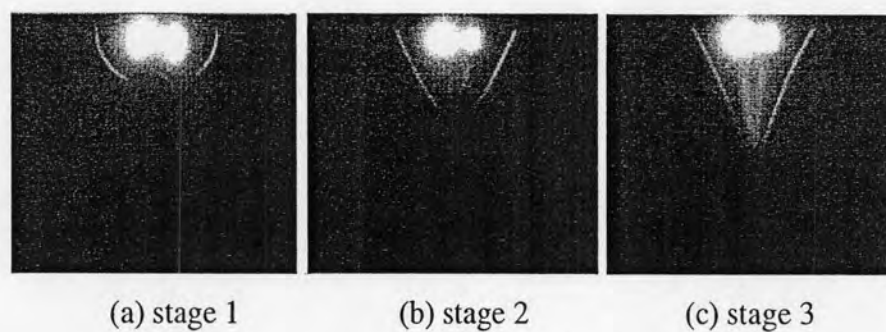
Due to the electric field, charge separation will take place in a droplet that is electrically conductive. Where the needle is positively charged, for instance, the positively charged species migrate to the surface of the droplet and the negatively charged species accumulate in its interior until the electric field within the liquid droplet is zero. Charge separation will generate a force that is countered by the surface tension within the droplet. The velocity at which these ionic species move through the liquid is determined by the magnitude of the electric field and the ionic mobility of the species. The stability of an electrically charged droplet at the end of a needle requires the inward surface tension forces to exceed the outward repulsion

force of like charges accumulating on the droplet surface [55]. However, Rayleigh (1996) calculated the maximum amount of charge which a drop of liquid can hold before the electrical forces overcome the surface tension of the droplet.

#### 2.4.1.2 Taylor's cone formation

When the polymer solution is charged, deformation of charged droplet under an electric field changed from a spherical pendant droplet to hemispherical and then to a conical shape, which normally terms "the Taylor's cone". Taylor [56] determined the equilibrium in conical form under the force between the electric field and surface tension to be achieved when the half angle of the cone was  $49.3^\circ$ . The formation of the Taylor cone is shown in Figure 2.5. This "Taylors cone" is formed at the critical voltage  $V_C$  applied to a droplet at the end of a needle of length  $h$  and radius  $R$  (Taylor 1969):

$$V_C^2 = (2L/h)^2(\ln(2h/R) - 1.5)(0.117\pi RT)$$



**Figure 2.5** Formation of the Taylor cone. Electric potential increases with each stage until equilibrium between surface tension and the electrical force is achieved in stage 3 [49].



### 2.4.1.3 Launching of the jet

The jet is the region beyond the base where the electrical forces continue to accelerate the polymer solution and to stretch the jet and this jet is initiation to occur from the surface layer of the cone. Due to copious entanglement of polymer chains in concentrated solution, the force available to a droplet via coulombic repulsion will generally be insufficient to explode it. However, the surface area must be increased to build the charge on the jet surface and this occurs through the formation of fibers. A slender fiber emanates from the cone to create additional surface area needed to accommodate surface charges, and it initially travels directly towards the grounded collector. This is partly due to surface shear forces generated by the potential difference between the base and the tip of the Taylor's cone.

### 2.4.1.4 Elongation of the straight segment

The beginning of jet will happen immediately when applied electric potential much more than  $V_c$  to the polymer solution. The coulombic repulsion of surface charges on the jet line to be composed of axial route that the jet line will be elongated to collector. The velocity of jet line will change, when distance is increased from Taylor's cone, the causes diameter of jet decreases rapidly length increases due to both extension and evaporation of the solvent. The initially a stable straight jet tapers down as it accelerates toward the collector by a high electrical potential applied between the solution and the collector, and tapering is pronounced in the region below the Taylor's cone. As the jet thins, the surface area per unit mass of jet material increases while the surface charge per unit area decreases. If the polymer is in the form of a solution in which the solvent has a high vapor pressure, evaporation of the solvent from the jet may reduce the mass flow velocity. The taper of the jet is also affected by solvent evaporation, since loss of the solvent can have a large effect on the viscoelasticity of the liquid polymer [56]. However, solvent evaporation continually increases the surface charge per unit area, driving the increase in surface area through extension.



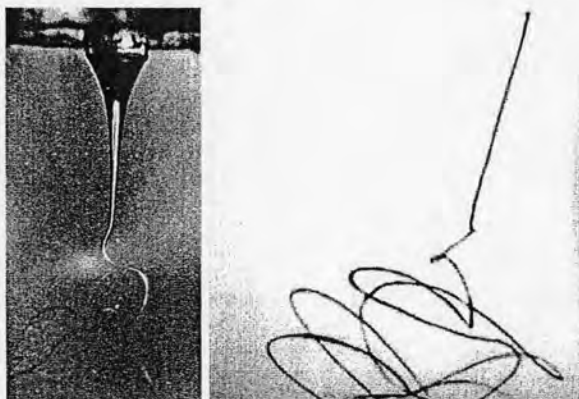
### 2.4.1.5 Whipping instability region

After a charged jet is ejected from the droplet of conical shape, it flows continuously under the influence of the electric field. There are two kinds of electrostatic forces acting on a jet segment. One is from the external field that reacts with charges present in a jet segment and the other from the coulombic repulsion between adjacent charges of similar polarity. The first force is responsible in the carrying the charged jet towards the collector and the second is responsible for the stretching of the charged jet. The coulombic repulsion can also cause different types of instability such as bending and splitting instability. The jet followed a bending, winding, spiraling and looping path in three dimensions as shown in Figure 2.6. The jet in each loop grew longer and thinner as the loop diameter increased, a direct result of the longer path length. After some time, segment of a loop suddenly developed a new bending instability, but at a smaller scale than that of the first one. Each cycle of bending instability can be described in three steps.

Step 1: A smooth segment that was straight or slightly curved suddenly developed an array of bends.

Step 2: The segment of the jet in each bend elongated and the array of bends became a series of spiraling loops with growing diameters.

Step 3: As the perimeter of the loops increased, the cross-sectional diameter of the jet forming the loop grew smaller, the conditions of the first step were established on a smaller scale, and the next cycle of bending instability began.



**Figure 2.6** Trajectory of the jet in the instability region. [58]

This cycle of instability is observed to repeat in a smaller scale. It was inferred that a larger number of cycles occurred resulted in a decrease in the jet diameters, hence a decrease in the diameter of the obtained fibers. The fluid jet solidifies as it dries and the fibers are collected some distance below the envelope cone [59]. In electrically driven bending instability, alternatively referred to as whipping instability, the jet rotates in a conical region, whose vertex is the end of the straight jet. The other end of the jet, which is highly stretched and reduced in diameter, is deposited on the collector as a result of the fast bending instability motions [60]. The different forces acting on the whipping charged jet during electrospinning can be described: Gravitational force  $F_G$  (towards the collector in a vertically arranged apparatus), the force is dependent on density of solution.

$$F_G = \rho \pi r^2 g$$

where  $\rho$  is the density of the liquid and  $g$  is the acceleration due to gravity.

The electrostatic force  $F_E$ , which extends the jet and tends to move it towards the grounded collector. The force is determined by the applied electric field and material characteristics. Coulombic repulsion forces  $F_C$  on the surface of the jet, which introduce instability and whipping motions. The magnitude of  $F_C$  is dependent on characteristics of the polymer and solvent. Viscoelastic forces, which work against the elongation of the jet in the electric field. This depends on the polymer molecular weight, the type of polymer, and the solvent. Surface tension forces, which work against the stretching of the jet and this depends on solvent type and polymer. Fractional forces between the surface of the jet and the surrounding air.

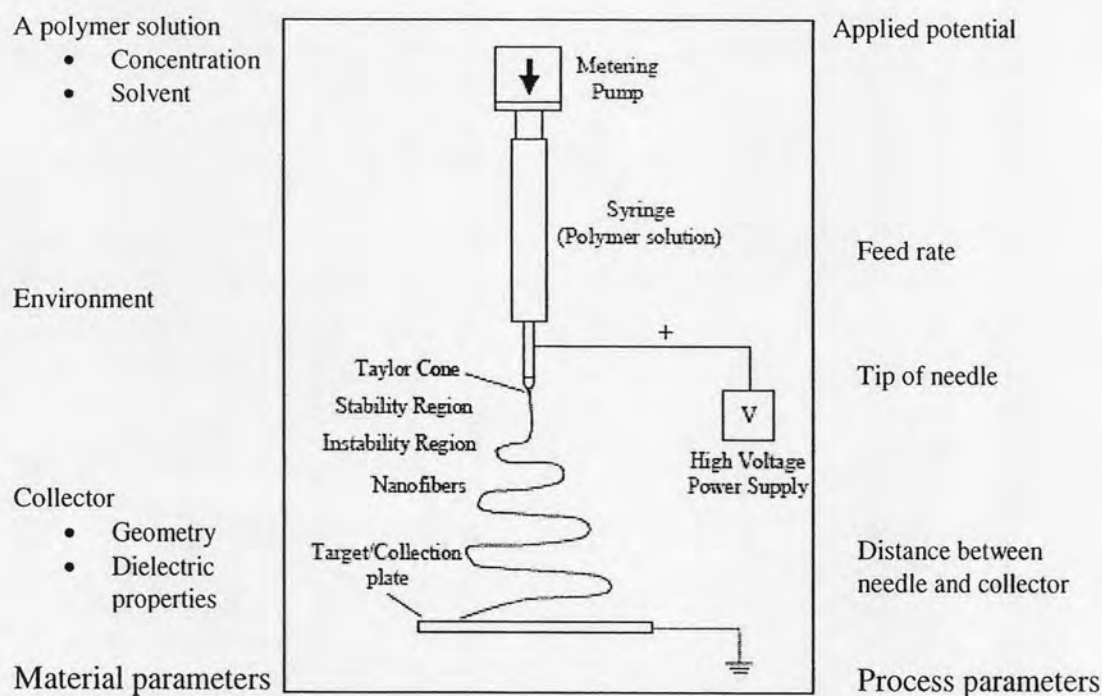
#### **2.4.1.6 Solidification into nanofiber**

The duration of jet to undergo whipping instability is controlled by the rate of evaporation of the solvent. With the evaporation of high pressure solvent, the elongational viscosity of the jet may result in the rapid deformation in the whipping instability state. As such, the fibers are thicker. Solvent volatility is

therefore a key consideration in controlling fiber diameter. With appropriate selection of solvents and process parameters, extremely fine fibers can be electrospun.

### 2.4.2 Parameters of electrospinning process

A proper choice of processing parameters that affect on the morphology and properties of electrospun fibers. There are many parameters that will influence the morphology of the resultant electrospun fibers such as the surface tension, the viscosity, the concentration of the solutions, molecular weights, applied electric fields distance between needle and collection screen, diameter of needle and flow rate of polymer solution. Two classes of variables that affect electrospinning can be identified from the literature: the material variables pertaining to either the choice of equipment or the operating parameters, material variables and process variables [55] as shown in Figure 2.7.



**Figure 2.7** The basic materials and process variables in electrospinning of polymer nanofibers.

#### **2.4.2.1 Concentration of solution**

The concentration or viscosity allowing adequate chain entanglement, continuous uniform fibers can be electrospun from polymer solution in a strong enough electric field and also affects much on the diameter of fibers. The viscosity increased, the spinning drop changed from approximately hemispherical to conical, the length of the jet increased as well. Fiber diameter also increased with solution viscosity and was approximately proportional to jet length [54].

#### **2.4.2.2 Solvent**

In the electrospinning process of a polymer solution, solvent is one of the main contributors influence the morphological appearance and electrical resistance. The obtaining morphology of fibers was depended on solvent evaporation during spinning. In order to choose of solvent we have to concern about conformation of the dissolved polymer chains, ease of charging the spinning jet, cohesion of solution due to surface tension forces and rate of solidification of the jet on evaporation of the solvent.

#### **2.4.2.3 Electric potential**

Applied electric potential provides the surface charge on the electrospinning jet and affected on morphology and diameter of fibers. With increasing electric potential, the polymer jet was discharged with a greater electrostatic repulsion that caused it to undergo instability and straight of jet. This resulted in the decrease of the fiber diameter. However, the effects of applied electric potential on morphology and diameter of fiber need to be considered together with other parameters, particularly the flow rate and the distance between the needle and the collection screen [54].

#### **2.4.2.4 Distance between the needle to the collector**

Varying the distance between the needle and the collection screen will have a direct influence on both the time available for evaporation of the solvent before the fiber reach the collector surface (flight time) and the strength of the electric field [54]. The electrospinning jet must allowed time for most of the solvent to be evaporated. When the distance between the needle and the collection screen is reduced, the jet will have a shorter distance to travel before it reaches the collector. Moreover, the electric field will also increase at same time and this will increase the acceleration of the jet to the collector. As a result, they may not have enough time for the solvents to evaporate when it hits the collector. When distance is too low, excess solvent may cause the fiber to merge where they contact to form junctions resulting in inter and intra layer bonding [54]. Moreover, increasing the distance results in a decreased in the average fiber diameter.

#### **2.4.2.5 Diameter of needle**

The internal diameter of the needle has a certain effect on the electrospinning process. A smaller internal diameter was found to reduce the clogging as well as the amount of bead on the fibers. The reduction in the clogging could be due to less exposure of solution to the atmosphere during spinning. Decrease in the internal diameter of the needle is also found to cause a reduction in the diameter of fibers. When the size of the droplet at the tip of the needle is decreased, the surface tension of the droplet increases. For the same electric potential supplied, a grater columbic force was required to cause jet initiation. As a result, the acceleration of jet decreases, and this allows more time for the solution to be stretched and elongated before it was collected. However, if the diameter of the needle is too small, it may not be possible to eject a droplet of solution at the tip of the needle.



#### **2.4.2.6 Flow rate of solution**

This is the rate at which the polymer solution is pumped into the tip to generate the Taylor's cone. Ideally, the flow rate must match the rate of removal of solution from the tip. At lower flow rate may only be intermittent with the Taylor's cone being depleted, but at higher flow rate under conditions where applied electric potential is not a limiting factor results in the average fiber diameter increasing with the flow rate.

However, the effects of applied electric potential, the flow rate, diameter of the needle and the distance between the needle and the collection screen need to be considered together.