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## Advances in Electroactive Electrospun Nanofibers

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### 1. Introduction

The first detailed description of the technique known nowadays as electrospinning dates from 1930's when Anton Formhals filed a patent entitled "*Process and Apparatus for Preparing Artificial Threads*". His patent described the formation of artificial filaments when a polymer solution or melt is submitted to a high strength electric field. Recently, with the emerging of nanotechnology, electrospinning was rediscovered and became an important method for producing ultrathin polymer fibers with diameters down to the nanometer scale. Many classes of polymers have been electrospun, opening up new promising applications such as in filtration, protective clothing, scaffolds for tissue engineering and a myriad of other possibilities.

Contrasting with the most common fiber processing techniques like melt spinning, dry spinning, wet spinning and extrusion; electrospinning is able to produce ultrathin fibers with very high surface area. This is of particular interest in sensors, actuators and other electroactive devices, especially when conducting polymers are used. Many kinds of conducting polymers have been used to produce electroactive polymer devices based on nanosized electrospun fibers as polyaniline, polypyrrol, polythiophene, among others. Although the available literature on electrospinning of polymer mats is extensive, there are few reports on electrospinning of electroactive polymers and their related applications.

In this chapter, special topics involving the production of electroactive nanofibers by electrospinning and their use in electroactive devices such as sensors, actuators, electroluminescent devices, conductive membranes and others are reviewed. Especial attention to processing parameters and effects of electroactive polymer structure and

properties in solution will be given. Finally, some perspectives on electrospinning of electroactive nanofibers obtained by electrospinning and their uses will be considered.

### 1.1 Historical background and current technologies

Electrospinning has emerged as one of the techniques that can be successfully used to produce polymeric fibers, mats and scaffolds down to the nanometer scale. Besides, electrospinning has been currently cited in an enormous amount of scientific papers and reports that show how it can be used to produce a vast number of morphologies with many potential applications. The development of this technique started with the studies of William Gilbert in the late 1600's, with the attempt to describe the deformation of water droplets under magnetic and electric fields. Later, in the 1880's, Lord Rayleigh was the first to estimate theoretically the pressure resulting from a charge  $q$  on a droplet of spherical radius  $r$  and surface tension  $\sigma$ . When the amount of charge  $q$  overcomes the Rayleigh limit  $q_r$ , the natural quadrupolar oscillation becomes unstable and the liquid spread out in fine jets [1]. The Rayleigh limit can also be reached by the liquid evaporation. The ejecting event is frequently called Rayleigh discharge or Coulomb fission and more commonly electro spray [2].

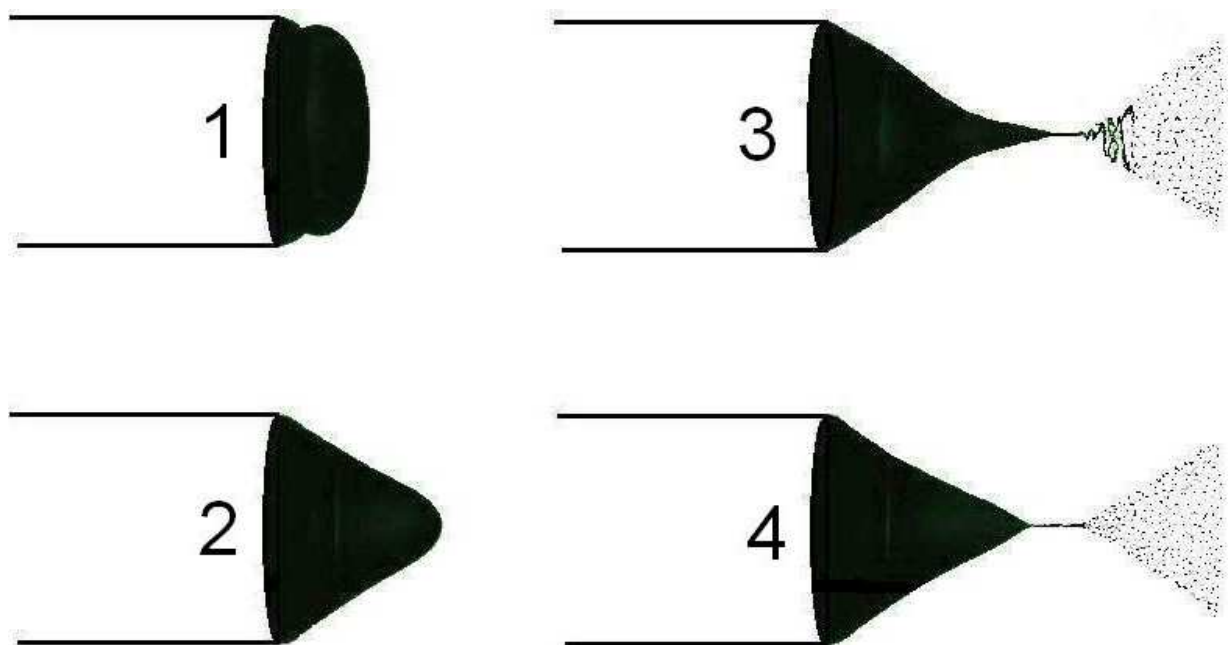


Fig. 1. Representation of liquid surface deformation with the increase of applied voltage (1-4), able to generate electro spraying.

Later in 1914, John Zeleny described that electrical discharge of liquid points consisted of acidulated water placed in a metal bar [3]. By the use of a refined experimental technique, Zeleny was able to measure the electric intensity at the surface of liquid droplets before and during the electrical discharge, leading to a better understanding of liquids surface instabilities due to the presence of electrical charges. In a paper published in 1917, Zeleny also observed that when electrification is increased to a certain limit value, depending on liquid surface tension and the curvature of its surface, the liquid surface becomes unstable, due to the inside pressure becomes equals to the outside pressure, and any slight accidental

displacement may result in a rapid and intense deformation of liquid surface. Above this critical condition, in case of further increase in electric density, the liquid is ejected under forms of fine threads which can eventually be broken into small drops [3].

At that time, some speculations on applying electrospray for viscous fluids arose. Later, this process became known as electrospinning and the process of spinning fine threads by the use of electrical charges was firstly patented by J. F. Cooley in February 1902 (U.S. Patent 692,631) and by W. J. Morton in July of the same year (U.S. Patent 0,705,691). In fact, the patent filed in 1934 by Anton Formhals (U.S. Patent 1,975,504) entitled "Process and Apparatus for Preparing Artificial Threads" is widely known as the first document which effectively consider the production of fiber threads by means of electric fields. This work was succeeded by a sequence of patents from 1934 to 1944 (U.S. Patent 2,349,950) and Formhals established a very precise experimental setup for producing electrospun fibers.

It is worth noting the fabulous work of Sir Geoffrey Taylor, from 1964 to 1969, who published various papers detailing the theoretical underling on disintegration of water drops under electric fields, including electrical force calculation on fine jets under strong electric fields and the deformation of liquid surfaces by an electrical field into a characteristic shape that is currently known as Taylor cone [4].

The term electrospinning was mainly popularized by Dr. Darrell H. Reneker in early 1990 in demonstrating that many types of polymers can be spun by means of electrostatic forces into fine threads known as micro or nanofibers depending of their diameters. Today, thousands of scientific papers and patents have been published on electrospinning. Besides fascinating many scientists around the world, this topic involves both scientific and technologic developments and includes many fields of the human knowledge such as physics, chemistry, material science and engineering, biology, biochemistry.

## **2. Nanofibers of conducting polymers**

### **2.1 Introduction to conducting polymers**

Conducting polymers have been used in a variety of applications. These materials exhibit the ability to allow the passage of electric current, store charge or display redox activities. Common polymers are mostly dielectric and can be modified in order to conduct electric current by the addition of conducting fillers, as metal powders, carbon black and other conductive materials. These filled polymers are commonly called Extrinsic Conducting Polymers - ECP's and can be used as, pressure sensors, actuators, electromagnetic interference (EMI) shielding etc. [5]

On the other hand, polymers formed by chains that contain conjugated chemical double bond, with a minimal molecular size able to produce electrical conductivity, are usually called Intrinsically Conducting Polymers - ICP's or simply conducting polymers. These materials formed by organic molecules containing conjugated chemical bonds such as aromatic rings and (or) conjugated oligomeric (or) polymeric conjugated oligomeric/polymeric chains have attracted enormous attention from scientists because of the possibility of their utilization in the development of electronic devices. Depending on the size of the molecule and its conjugation extension, interesting physical and chemical properties may arise - electrical conductivity, electroluminescence, electrochromism - which may be used in several practical applications, such as static charge dissipation,

diodes and light emitters, memory storage, rechargeable batteries, chemical and biological sensors [6-9].

The first attempt in obtaining polymers with conjugate chemical bonds (polyenes) dates from 1958 through the polymerization of acetylene by Natta and coworkers [10]. The obtained polyene was widely accepted as consisted of a long conjugated polymer chain. Theoretical speculations on electrical properties of Polyacetylene – PAC, indicated a metallic conducting behavior in an alternate double bonded linear chain. However, at that time there was no clear idea if a long polyene chain would be energetically more stable than that with bonds of equal lengths (delocalization).

Using an adapted synthetic route proposed by Natta, Shirakawa and coworkers [10] synthesized polyacetylene in the 1970's. This polymer was obtained as a smooth film with metallic brightness and relatively low conductivity, ranging from  $10^{-8}$  to  $10^{-7}$  S.cm<sup>-1</sup>, for *cis*-polyacetylene, to  $10^{-3}$ - $10^{-2}$  S.cm<sup>-1</sup>, for *trans*-polyacetylene. Simultaneously, MacDiarmid and Heeger [11] were investigating an inorganic polymer, poly(sulfur nitride) – SN<sub>x</sub>, which has exhibited electrical conductivity between 10 and 1,700 S cm<sup>-1</sup> at room temperature and superconductivity at low temperatures (~0.26K). Later, in 1977, Shirakawa, MacDiarmid and Heeger [12] performed a modification in the previous preparation procedure of *trans*-polyacetylene, introducing small amounts of iodine, which is known for its high oxidizing strength. The polymer obtained through this new procedure exhibited high electrical conductivity,  $10^3$  S.cm<sup>-1</sup>, that was attributed to the presence of charge carriers formed upon oxidation of the conjugated chemical bonds of the polymer backbone. The oxidation was called “doping” in analogy to semiconductors.

Conjugate polymers are considered one of the most innovative materials and different types are available nowadays, since a great number of compounds is used as monomers and different synthetic routes can be adopted for this purpose [13,14]. All the synthetic routes developed so far can be grouped into two main types: chemical and electrochemical synthesis. Enzymatic [15] and plasma synthesis [16] of conjugated polymers have also been reported. Processing in conducting polymers is another important issue that needs to be considered. Such materials can mostly be obtained in an easy and controllable way. They are chemically and thermally stable even in the conducting state, and exhibit high electrical conductivity which can be controlled according to different doping methods [13,17]. Since the discovery of conducting polymers, this research area has witnessed the increasing number of conjugated polymers with improved solubility that can be processed by different techniques. Table 1 shows some examples of these polymers.

Techniques used for processing conjugated polymers should take advantage of their physical and chemical properties in order to produce structures with elevated organization and transparency depending on the method of fabrication and end use.

## 2.2 Electrical conduction and doping in conjugated polymers

Electrical conductivity is a physical property that can vary several orders of magnitude, ranging from  $10^{-22}$  S cm<sup>-1</sup> for the best insulators up to  $10^{10}$  S cm<sup>-1</sup> at 1K for the best conductors. Semiconductors exhibit intermediary conductivity, between  $10^{-7}$  and  $10^{-3}$  S cm<sup>-1</sup>, once the energy gap between conduction and valence band is of the order of few electrons volt (eV). Depending on the type of polymer, doping level and dopant, conductivity of conjugated polymers varies over a broad range of conductivity as can be seen in Figure 2.

Polymer name	Chemical structure	Polymer name	Chemical structure
<i>Trans</i> -polyacetylene ( <i>trans</i> -PAC)		Polypyrrole (PPy)	
Poly( <i>p</i> -phenylene) (PPP)		Polythiophene (PTh)	
Poly( <i>p</i> -phenylene-vinylene) (PPV)		Poly(3,4-ethylene dioxothiophene) (PEDOT)	
Poly( <i>p</i> -phenylene-sulphide) (PPS)		Polyaniline (PAni)	
Polyfurane (PFu)		Polycarbazole (PCbz)	

Table 1. Examples of the most common intrinsically conducting polymers (ICP's).

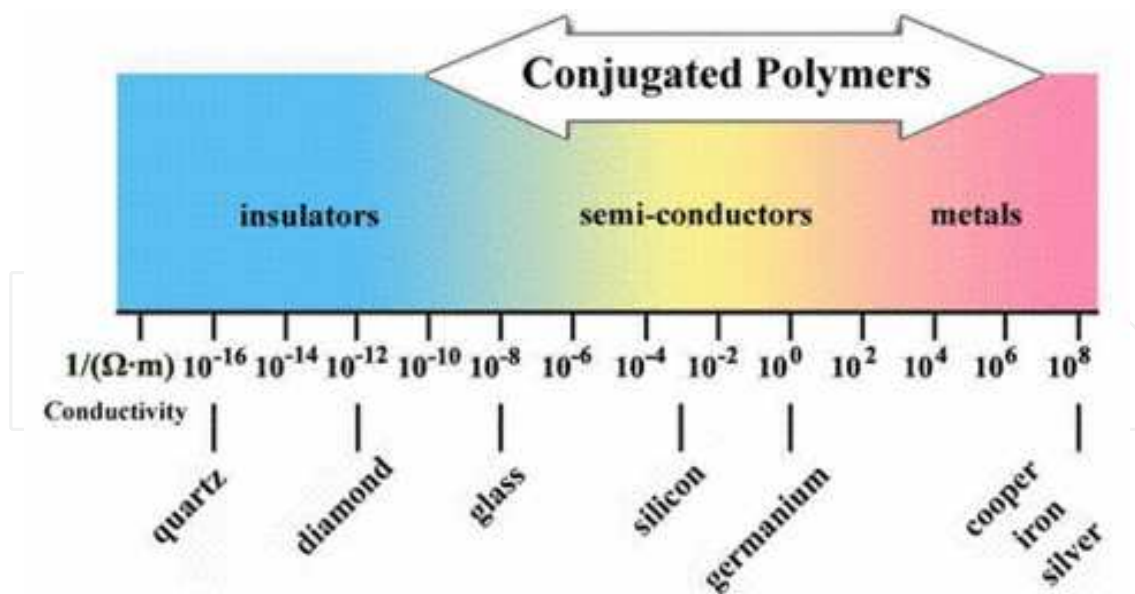


Fig. 2. Schematic illustration of conductivity range of conjugated polymers compared with most common materials. (source: The Nobel Prize in Chemistry, 2000, www.nobelprize.org)

As already mentioned, conjugated polymers are formed by a main backbone containing alternating single and double chemical bonds known as conjugation. Whereas a single bond (or sigma bond,  $\sigma$ ) is strong and contains strongly localized electrons under a  $sp^3$  orbital

symmetry, a double bond (or pi bond,  $\pi$ ) is weaker and electrons are less localized following a  $sp^2$  orbital symmetry. This means that  $\pi$  electrons may exhibit higher mobility when compared to  $\sigma$  electrons and can move along the backbone since the conjugation leads to the formation of extended delocalized orbitals.

One can imagine that because of this conjugated configuration polymers are electrical conductors. However, for conjugated polymers to become conducting, an extra electron needs to be removed from the backbone in order to create a vacancy, through a redox process called doping. In fact, the first results obtained by Shirakawa's group [5] showed that pristine polyacetylene had conductivity values around  $10^{-3} \text{ S cm}^{-1}$ , a semiconductor. The vacancy or "hole" is a position where an electron is missing in the valence band. If a neighboring electron jumps into the hole a new hole is generated from where the electron jumped and this process perpetuates allowing charge to migrate a long the polymer backbone, which is in fact the electrical conduction [18].

Many different theoretical models [19] have been already proposed to address the electrical conduction exhibited by conjugated polymers after doping. However, a band model is usually referred to because it is able to explain many of the phenomena related in such systems. According to the band model, it was initially believed that during doping valence electrons were removed from the valence band (the highest occupied molecular orbitals – HOMO) and added to the conduction band (the lowest unoccupied molecular orbitals – LUMO) like in a HOMO-LUMO transition. Nevertheless, this hypothesis did not predict the existence of charge carriers with a null spin and it had to be reformulated.

In the case of polyacetylene, structural defects (or free radicals, in a chemistry terminology) are generated during the synthesis of the polymer due to oxidation/reduction reactions. Such defects were called solitons, but they are still unable to perform the electrical conduction due to the energy associated to its transition to conduction band to be around 1.4 eV and, therefore, thermal energy is not enough to promote electrons to the conduction band. After the doping process, which is basically a process where electrons are removed from or added to the polymer, charged solitons are generated; these are the carriers responsible for the electrical conduction. Charged solitons are species with a null spin and, hence, one concludes that the electrical conduction in polyacetylene is based on fully occupied bands in the ground state [18,19]. Figure 3 represents band energy levels of possible solitons configuration, i.e., positive, neutral and negative soliton according to their spin properties. In fact, solitons are not created separately. A soliton / anti-soliton pair is always created after redox process in a conjugated polymer chain. Figure 4 illustrates the soliton soliton / anti-soliton separation process when polymer chains are submitted to an external electric field.

The proposed theoretical model for polyacetylene is, however, unable to explain the electrical conduction in aromatic and heteroaromatic conjugated polymers, mainly due to the existence of other types of carriers in such polymers. The removal of an electron from these polymers is accompanied by a local distortion in the crystal lattice, which may be represented by a conversion of the aromatic rings from the benzenoid to the quinoid form. As the quantized states of crystal structures can be expressed in terms of phonons, this electron-phonon coupling is called polaron and represents a different type of charge carrier in conjugated polymers. The quinoid form has a lower formation energy and higher electron affinity than the benzenoid form. Therefore, during the doping, the charge accommodation in the polymeric chain is energetically favored by a combination of oxidation reaction and chain distortion [20].

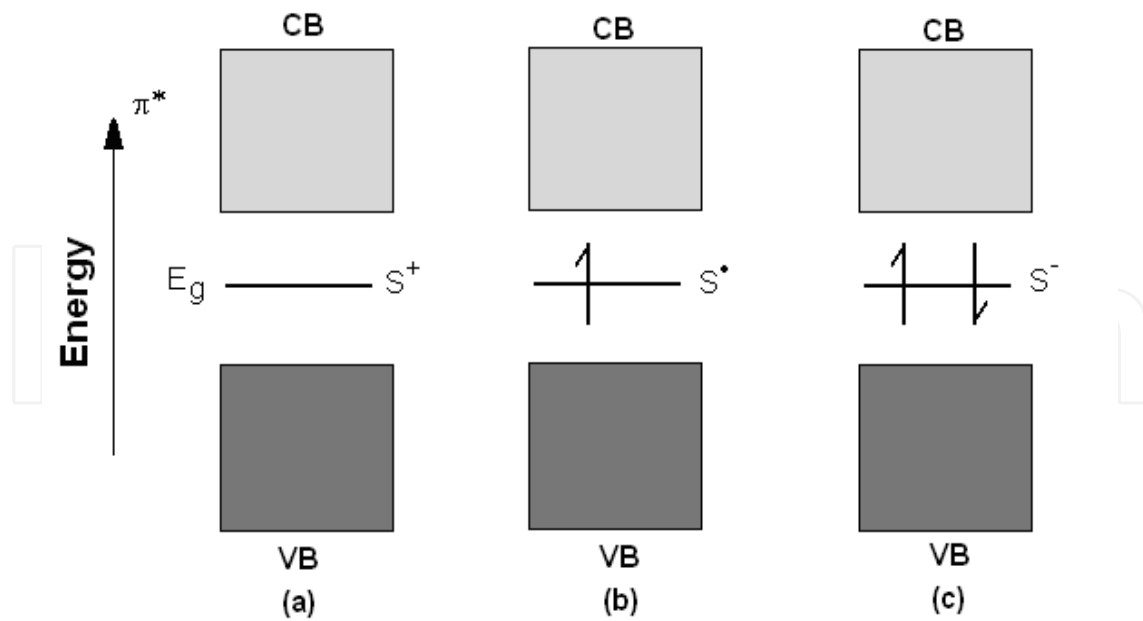


Fig. 3. Positive (a), neutral (b) and negative (c) solitons. Solitons are located in an energy level equivalent to the half of the gap size. Positive and negative solitons are formed through p-doping and n-doping process, respectively. Both are null spin entities [5].

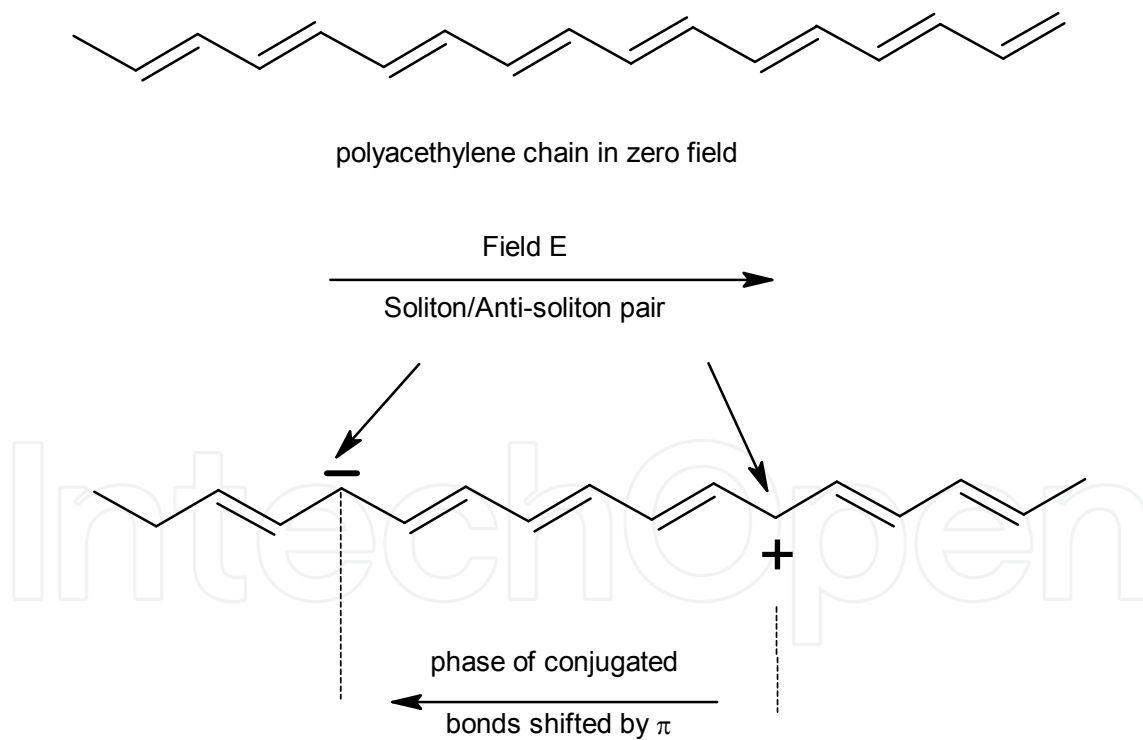


Fig. 4. Schematic representation of soliton - anti-soliton separation and electrical conduction in Polyacetylene chain. (source: <http://electrons.wikidot.com>).

As mentioned before, a polaron is considered as a positive charge carrier formed by the electron-phonon coupling and, in a chemistry definition, is a radical-cation with  $\frac{1}{2}$  spin moment and two electronic states. Both states are located around the Fermi level of the polymer with the lower energy state being occupied by one electron. When the doping level



increases such states are broadened forming semi-filled conduction bands. The removal of a second electron can be performed and leads to the formation of a bipolaron which is defined as a pair of positive charges associated to a stronger lattice distortion. Bipolarons also form two bands but both are empty resulting in a Fermi level close to the maximum of the valence band [18-21]. Figure 5 represents the energy levels of doped polypyrrol with respective levels of polaron and bipolaron charge carriers.

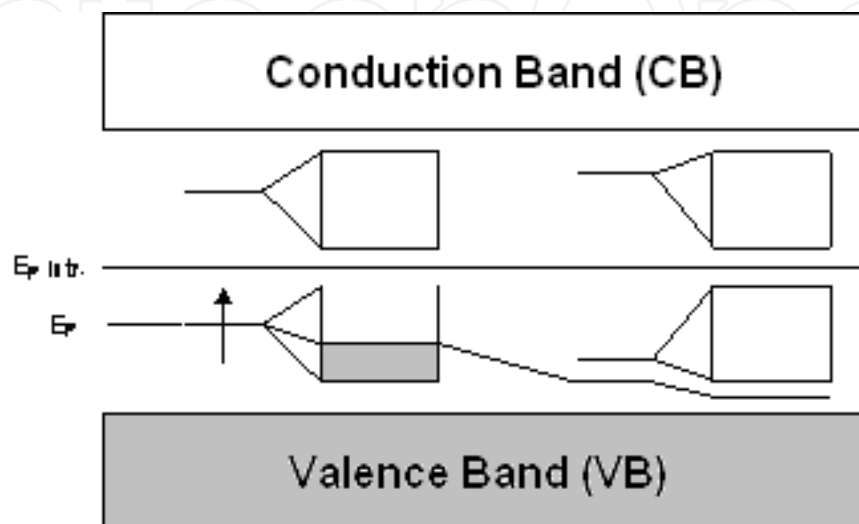


Fig. 5. Scheme of energy levels of doped polypyrrol with polarons and bipolarons [21].

Assuming those models to explain the electrical conduction in conjugated polymers, doping methods have been developed in order to produce conjugated polymers with high conductivity. Although there is still a current search for doping methods able to produce polymers with elevated conductivity, many of the technological applications proposed for conjugated polymers do not demand highly conducting materials and hence, the semiconducting behavior of these polymers has been more often exploited [13,22].

Doping is the term used to define the process where a material, insulator or semiconducting, is converted into an electrical conductor. In a general sense, the doping process is based upon the removal or addition of electrons from/to a material which can be carried out in different ways. In the case of inorganic semiconductors, doping is represented by the addition of small amounts ( $10^{-5}$ - $10^{-8}$  atoms of dopant per atoms of the material) of a doping agent or dopant, which replaces atoms from the original material. Differently from that, doping of conjugated polymers demands larger amounts of dopants ( $10^2$ - $10^1$  moles of dopant per moles of monomer) but there is no replacement of atoms. The doping process in conjugated polymers is based on chemical reactions between the dopant and the polymer, usually oxidation/reduction reactions in which the initially neutral polymer is converted into a charged macromolecule whose charge is compensated by a counter-ion original from the dopant. According to MacDiarmid [13] there are three main types of doping process that can be applied to conjugated polymers: (a) redox doping; (b) doping without dopant ions and (c) non-redox doping.

In the first type, redox doping, the  $\pi$  bonds in a conjugated polymer undergo chemical or electrochemical oxidation/reduction reactions in which the number of electrons is changed. All conjugated polymers can be doped by this type of doping. If we consider the oxidation

of the  $\pi$  bonds, electrons are removed and therefore the polymer backbone exhibits a positive net charge which is balanced by the presence of a counter-ion of opposite charge (negative). Usually, this type of doping is referred as p-doping in analogy to inorganic semiconductors. This process can be carried out by a chemical dopant, such as iodine and other halogen compounds (Figure 6), or electrochemically by anodic oxidation of the polymer in a medium containing a salt, for instance  $\text{LiClO}_4$ . The counter-ions are, respectively, the reduced iodine ( $\text{I}^-$ ) and the perchlorate ion ( $\text{ClO}_4^-$ ). In the n-doping, the polymer backbone is reduced and electrons are incorporated either chemically or electrochemically. The n-doping was first achieved in trans-polyacetylene by treating it with sodium amalgam or sodium naphthalide. The electrochemical reduction can be performed in the presence of  $\text{LiClO}_4$  where  $\text{Li}^+$  is the counter-ion [13].

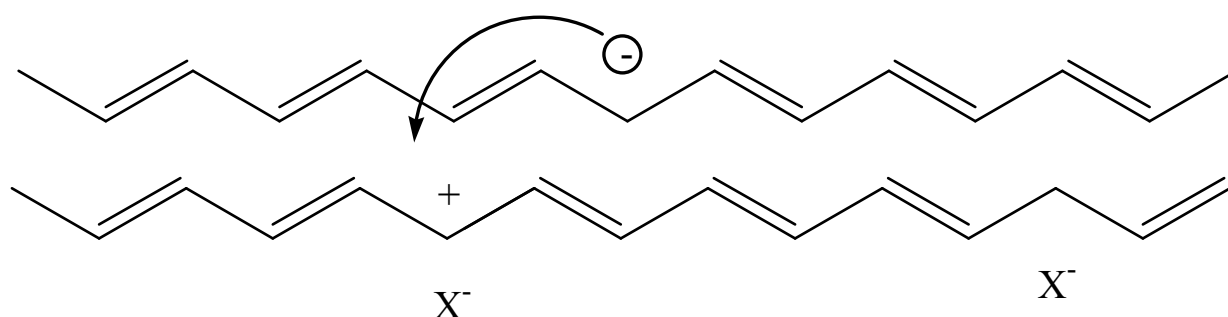


Fig. 6. Representation of charged solitons trapped by dopant counterions.

In a second type of doping, counter-ions are not incorporated into the polymer matrix where photo-doping and charge-injection doping may be considered. In the photo-doping conjugated polymer is exposed to a radiation source with energy greater than its band-gap and as consequence, electrons are promoted across the gap. If the polymer is kept under radiation and an electrical potential is applied, electrons and holes generated during photo-doping separate from each other and photoconductivity is observed. In order to succeed the charge-injection doping, a film of conjugated polymer is assembled onto the surface of a metal with a separating layer made of a dielectric material. When an appropriate electrical potential is applied to this configuration, a surface charge layer is formed on top of the polymeric film which induces the formation of charges on it, however, without the presence of a dopant ion [13].

The third type of doping, called protonation, is based on non-redox process what means that the number of electrons associated with the polymer backbone remains unchanged. This mechanism is based on acid-basic reactions and is observed exclusively in polyaniline and its derivatives. Briefly, the emeraldine oxidation state of polyaniline can undergo an acid-base reaction where the imine nitrogen atoms are protonated by a protonic acid, or Lewis acids, generating positively charge carriers, or polarons, without changing its oxidation state [13, 22-27].

### 2.3 Processing of electroactive polymers

When dealing with conjugated polymers, processing becomes a very important issue. For many years, these materials were considered intractable, since they often degrade before melting and show poor solubility in many common solvents, mostly due to their elevated aromaticity, high hydrogen bond density and low flexibility of polymer chains [28]. Many

efforts have been concentrated to improve conjugated polymer processability [29]. Monomer functionalization is one of the approaches used to obtain processable conducting polymers [30]. In order to be used in practical applications, a conjugated polymer must be cost-effective to be synthesized and purified, have good chemical and electrical stability, and easily processed from either solution or melt. The latter is the most problematic aspect of conjugated polymers.

Solubility in conjugated polymers has been improved with the synthesis of derivatives and also by using different combinations of dopants and solvents. For example, poly(*o*-ethoxyaniline (POEA) is a polyaniline derivative with improved solubility and processability due to addition of an ethoxy group at the ortho position of polyaniline aromatic ring. These two approaches have enabled, for example, the fabrication of thin films of conjugated polymers by different techniques. In the form of thin films, conjugated polymers are very adequate to be employed as sensitive layers, transducers and support for immobilization of different molecules in different device systems configurations [31]. Moreover, their performance might be enhanced to unimaginable levels when films with thickness around hundreds of nanometers are fabricated.

Many efforts have started to be made in order to produce materials at very low physical dimensions since many properties can be enhanced or even new properties can arise at the nanoscale level [32]. Some of the methods used to obtain these structures are Langmuir-Blodgett, layer-by-layer (LbL) deposition and spinning techniques.

### 2.3.1 Langmuir-blodgett

One of the most used techniques to produce nanostructures based on conducting polymers is the Langmuir-Blodgett approach. Langmuir-Blodgett technique (LB) was developed in 1935 by I. Langmuir and K. Blodgett pointing the production of monomolecular layers of fatty acids onto solid supports from an aqueous subphase [9,33]. Lately, this technique has been employed to fabricate films of many different materials, including conjugated polymers [34-36]. Among interesting features presented by the LB technique one can cite its ability in constructing ultra-thin films (of the order of nanometers) with structures whose molecular architecture could be manipulated and appropriately designed. Mono and multilayer films can be produced with a high degree of control of the film thickness and may even provide a high degree of orientational order [33-35]. In LB technique, generally, a solution of an amphiphilic molecule is spread over an aqueous subphase allowing the solvent evaporation. Thus, the molecules are self-organized with their hydrophilic parts pointing to the water surface. After, a moveable barrier is able to compress the molecules in a solid phase oriented film. Figure 7 represents Langmuir film orientation and Langmuir-Blodgett film deposition [37].

For the reasons exemplified above, several approaches have been used to process conjugated polymers in the form of LB films since they can be produced only in specific conditions. Among these approaches, mixing the conjugated polymer with a surface-active compound, use of polymer derivatives and polymerization in the Langmuir trough are the most investigated for conjugated polymer processing [34,35].

In the first approach, mixing, the conjugated polymer is mixed with a surface-active compound such as a fatty acid or a plasticizer. The resulting film is characterized by polymer molecules embedded into a well-organized matrix of fatty acid molecules (or plasticizer). Poly(alkyl thiophenes) and PANi derivatives, whose monolayers were too rigid to be transferred, have been processed by mixing [34,35].

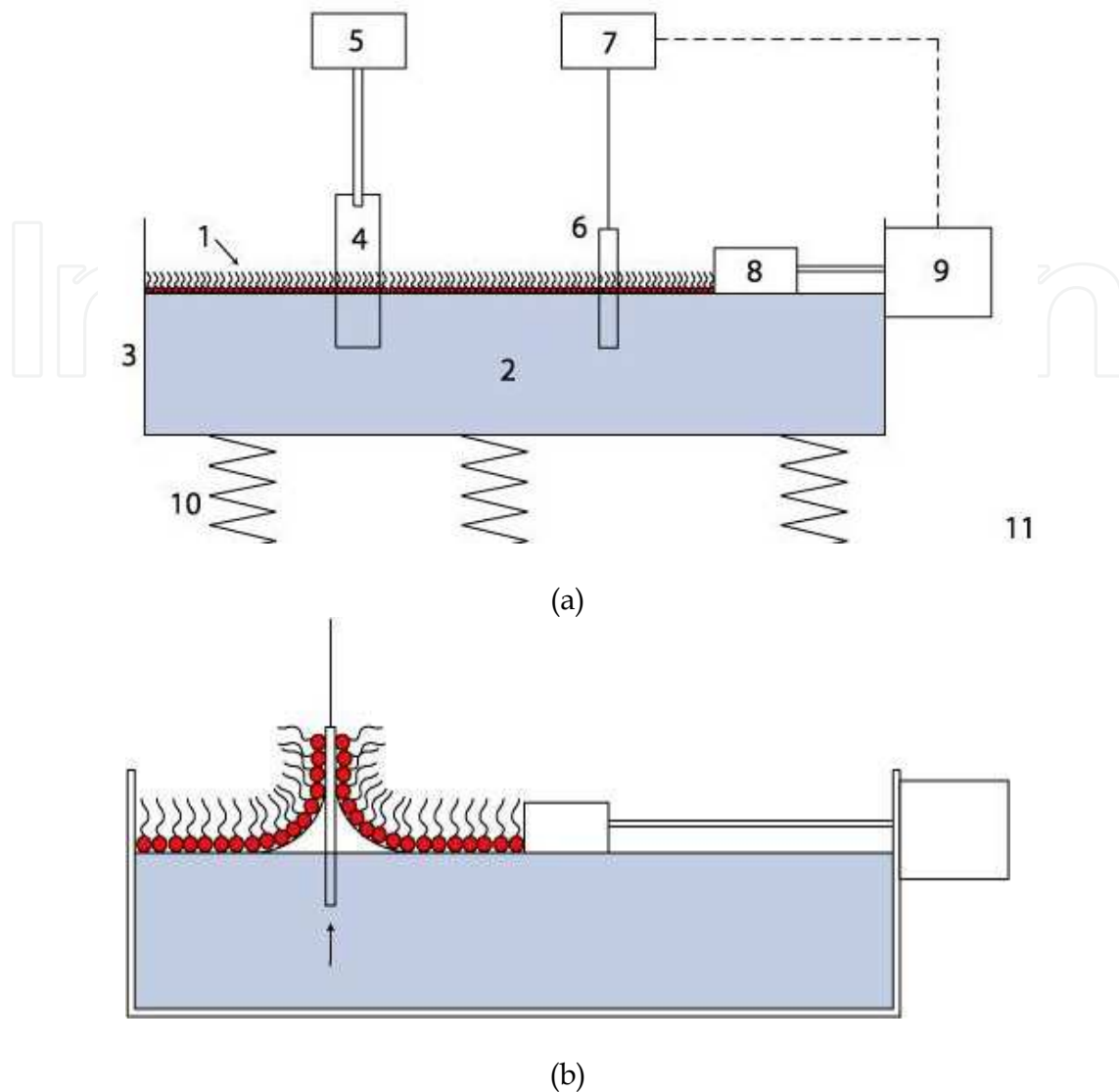


Fig. 7. (a) a schematic of a Langmuir Blodgett trough: 1. Amphiphile monolayer 2. Liquid subphase 3. LB Trough 4. Solid substrate 5. Dipping mechanism 6. Wilhelmy Plate 7. Electrobalance 8. Barrier 9. Barrier Mechanism 10. Vibration reduction system 11. Clean room enclosure; (b) monolayer transfer onto a substrate after film compression (source: <http://en.wikipedia.org/>).

Conjugated polymer derivatives are usually more soluble in common organic solvents and hence can be spread over an aqueous subphase. Good quality LB films from poly(*o*-alkoxyanilines) and pure poly(3,4-dibutoxythiophene) have been fabricated with no need for addition of surface-active compounds or processing aids [34-36].

In a third approach, Langmuir monolayers from the monomer are deposited followed by a subsequent in situ polymerization. Often, amphiphilic derivatives monomers are spread over the subphase which contains the polymerizing agent. Polymerization then occurs by interaction between the agent in the subphase and the film forming molecules. The polymeric monolayer would be subsequently transferred onto a solid support. LB films from PANi and PPy derivatives have been fabricated in this way. This approach can be further modified where the polymerization is carried out after the LB film deposition. The

LB film containing monolayers of a specific monomer is polymerized by thermal treatment, as in the case of poly(p-phenylenevinylene)s and polyacetylenes, electrochemical oxidation for films of pyrrole derivatives or exposure to UV light [34,35].

### 2.3.2 Layer-by-layer (LBL)

There are other interesting and promising approaches in producing nanometrically organized structures with conjugated polymers, one of them is called layer-by-layer technique or self-assembly. The layer-by-layer (LBL) deposition technique was originally proposed by Iler in 1966 [38] when dealing with the adsorption of colloidal particles. However, this technique was reformulated in the 80's by Sagiv [39] and extended to polyelectrolytes by Decher [40] in 1990. Although the LB technique is a promising and elegant way of producing thin films, its elevated cost and experimental procedure represent disadvantageous concerning the fabrication of films in large scale. In this sense, the LBL represents an alternative to the LB method mainly due to its low cost and easier experimental procedure.

LBL films are formed by the spontaneous adsorption of molecules from their solutions onto a solid support through different kinds of adsorption mechanisms. Basically, a chosen support is immersed into the deposition solution containing the material of interest for a pre-determined period of time and the molecules adsorb forming a layer. This layer has a thickness ranging from 10 to 100 Å. Later, the support is removed, washed and dried and, in a next step can be immersed again in the same solution or in a different one, if multilayer films are desired (see Figure 8). The solution is kept in a beaker and there is no need of a clean room. Any type of material like metals, glass or plastics and in different shapes such as spheres, slides or rods can be used as support to film deposition [41,42].

LBL films from different types of conjugated polymers have been fabricated and examples include PANi and its alkoxy derivatives [43-47], sulfonated-PANi [44], Polypyrrole [43], poly(thiophene acetic acid) [44] and poly(p-phenylene vinylene) [44]. In general, the adsorption of each layer contributes with the same amount of material to the film, which means that the film thickness can be controlled by the number of deposited layers. Moreover, the layer thickness can be varied by manipulating the polymeric solution parameters, such as pH, ionic strength and polymeric concentration. LBL films of conjugated polymers exhibit low roughness and their morphology can be controlled by the addition of different polyanions, such as sulfonated polystyrene, sulfonated lignin, poly(vinyl pyrrolidinone) and poly(allylamine hydrochloride). The polyanion presence can also play an important role in the stability of the conjugated polymer in the conducting state, since polyelectrolyte complexes are formed between them, which stabilize their charge and prevent proton loss in the case of PANi and its derivatives [48].

### 2.3.3 Spin coating

Spin coating and casting techniques have also been employed, mainly for soluble conjugated polymers and for their blends with conventional polymers. Spin coating can be considered as an improvement of casting film technique where a polymer solution is spread over an appropriate substrate and solvent is allowed to evaporate. A typical process involves deposition of small droplets of a polymer solution onto the center of a substrate and then spinning the substance at high speed. Thus, centripetal force will cause the spread of the substance over the substrate in the form of thin film. Evidently, the final thickness and

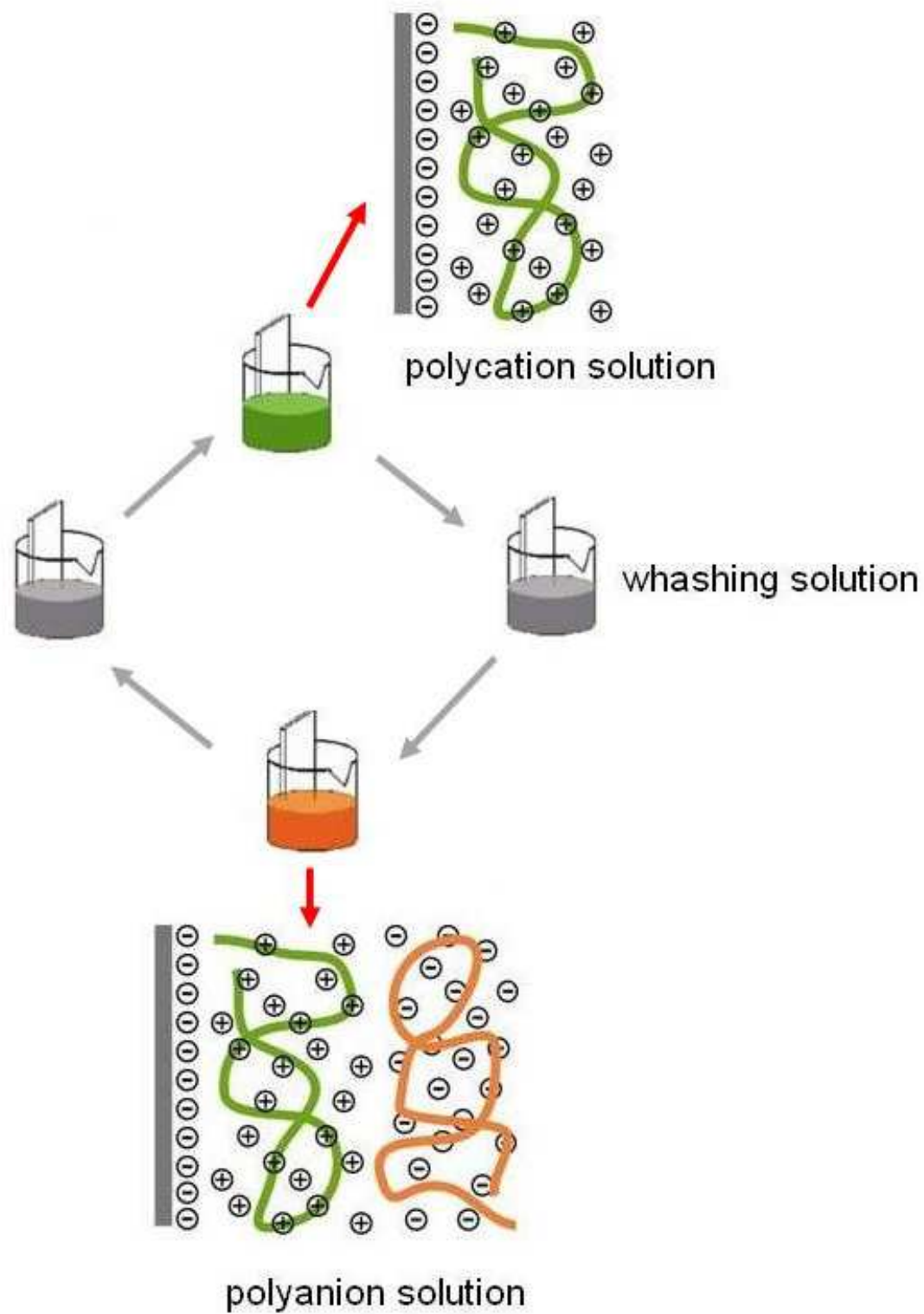


Fig. 8. Schematic of the film deposition by the LBL process.

other film properties will depend of the physical properties of the solution and process parameters. Spin coated, films can usually be obtained with thickness range around 0.1-200  $\mu\text{m}$  [49]. Figure 9 exemplifies the basic steps in spin coating process.

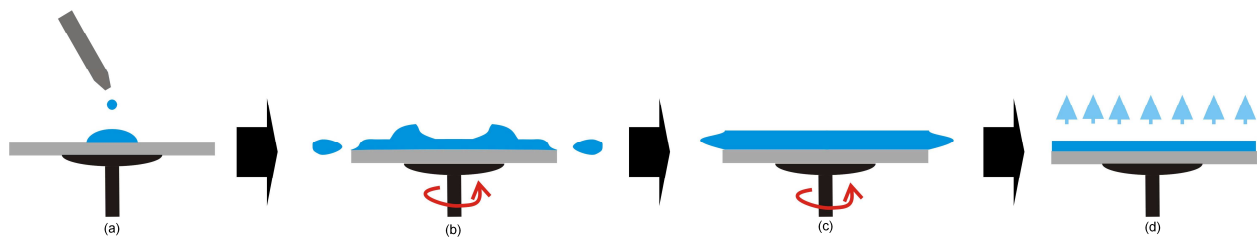


Fig. 9. Schematic illustration of spin coating process; (a) solution deposition, (b) substrate acceleration, (c) constant spinning rate (d) drying.

([http://www.freephotos.biz/images/science/chemistry/solgel\\_spincoating.jpg](http://www.freephotos.biz/images/science/chemistry/solgel_spincoating.jpg)).

Many studies have been done by using spin coating to produce thin films of conducting polymers, mainly for electroluminescent materials and devices [50-52]. Meier and coworkers reported the influence of film thickness on the phase separation mechanism in poly[(1-methoxy)-4-(2-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) and poly(Nvinylcarbazole) (PVK) spin coated films [53]. According to the authors, films with thickness from 16 to 61 nm were obtained by spin coating solutions with concentrations from 1 to 9 g L<sup>-1</sup> at 2000 rpm.

Spin coating is relatively simple and cost-effective and, furthermore, thin films with highly molecular orientations can be readily produced. Furthermore, the thickness of spin coated films are still greater than that obtained by LB and LBL, and the constant presence of solvents used for processing must be considered. Films with very low thickness, around hundreds of nanometers, are usually preferred in recent technological applications in order to assure new and unrelated properties due to size reduction [54].

### 2.3.4 Fiber production

Another very interesting and useful way to produce nanostructures of conducting polymers is the production nanofibers. Conductive materials in fibrillar shape may be advantageous comparing to films due to their inherent properties as anisotropy, high surface area and mechanical strength. Fibrous conductive materials are, for example, of particular interest in electroactive composites.

Fine metal wires, carbon fibers and carbon nanotubes have been efficiently distributed in an insulating polymer matrix in order to improve both electrical and mechanical properties [5]. Combination of electrical properties with good mechanical performance is of particular interest in ECP's technology. Fibers have intrinsically high structure factor which results in lower percolation threshold values avoiding material failure with low filler content. Also, the use of mechanically stronger fibers will result in stronger composites.

Some authors compare the electrical performance of conducting fiber composites to gelation process in a polymer after crosslinking, where the conductive network corresponds to the gel fraction. If a fiber segment is able to conduct it must be connected to the gel in both ends. In the case of low filler concentration, there is no conductive network. When the fiber content is increased until a three-dimensional network is firstly formed, the gel point is achieved and conductivity increases by a large factor [5]. If some processing technique is able to spatially orient the fibers, the conductive network will be formed at even lower concentrations, and the ECP will have good electrical performance associated to the plastic mechanical properties of the matrix.

Currently, there are many techniques able to produce polymeric nanofibers as, drawing, template synthesis, phase separation, self-assembly, solution blow spinning and electrospinning [55,56]. Ondarçucu and Joachim demonstrated the possibility of drawing polymer fibers down to the nanometer scale with the tip of a micropipette and a microdroplet of a polymer solution. The authors compared this process to dry-spinning at molecular level and nanofibers with dimensions comparable to carbon nanotubes can be drawn by this easy and inexpensive fashion [57]. Obviously, the drawing process requires a polymer with appropriate viscoelastic properties which are able to being deformed and kept connected by cohesive forces. Besides being simple and inexpensive, this technique is very limited for conjugate polymers, once most of them have lower solubility and form solutions with small viscous modulus.

In phase separation approach, a polymer is solubilized and then undergoes to gelation process. Due to the physical incompatibility of the gel and solvent, this is able to be removed and the left structure, after freezing, is obtained in nanofibrillar structures [55]. Template synthesis basically implies in the use of a template or mold to obtain a desired structure. Commonly metal oxide membranes with nanoporous are used, where a polymer solution is forced to pass through to a non-solvent bath originating nanofibers depending of the pores diameter [55].

A similar method was developed to obtain polyaniline nanofibrils in such way that growing polymer chains separate from solution according to their molecular size. According to Huang and Kaner [58], polyaniline nanofibers are observed to be formed spontaneously during the chemical oxidative polymerization of aniline. The authors observed that the key of the nanofibril formation is the suppression of the secondary chain growth that leads to agglomerated particles. Depending of the doping acid nanofibers with diameters values between 30 and 120 nm can be obtained by this approach. These nanofibrils can be used in as a template to grow inorganic/polyaniline nanocomposites that lead to exciting properties such as electrical bistability that can be used for nonvolatile memory devices [59].

Medeiros and coworkers successfully produced nanostructured films of poly(o-ethoxyaniline) (POEA) alternated with cellulose nanofibrils (CnF) by layer-by-layer assembly (LBL) at different pH values. According to the authors it was possible to build up films by alternating POEA and CnF layers with relatively precise architectural control by controlling the number of layers and pH. Film thickness had a dependence on pH which is a combination of the effects of the deposited amount for each POEA layer and the pH at which the absorption of the cellulose nanofibrils was carried out [60].

The same authors also produced conductive nanofibrils by *in situ* coating cellulose nanowhiskers with different thickness of polyaniline. One of the advantages of using these coated whiskers instead of pristine conjugated polymers is the inherent strong nature of cellulose allied with the conductive nature of polyaniline [61].

### 2.3.5 Solution blow spinning

A new technique called solution blow spinning has been developed as an alternative method for making non-woven webs of micro- and nanofibers with down to the nanometer scale with the advantage of having a fiber production rate several times higher [56]. This solution blow spinning method is based on the use of a syringe pump to deliver a polymer



solution connected to an apparatus consisting of concentric nozzles whereby the polymer solution is pumped through the inner nozzle while a constant, high velocity gas flow is sustained through the outer nozzle (See Figure 10). The aerodynamic forces are able to stretch the solution exiting the inner nozzle to produce long filaments with diameter down to the nanoscale.

With this technique the authors have been able to produce a variety of morphologies such as smooth and porous fibers as well as beaded fibers. Moreover, polymers such as PLA, PMMA, PEO, PS and PVC have been successfully used to produce micro and nanosized fibers with diameters as low as 40 nm [56, 62].

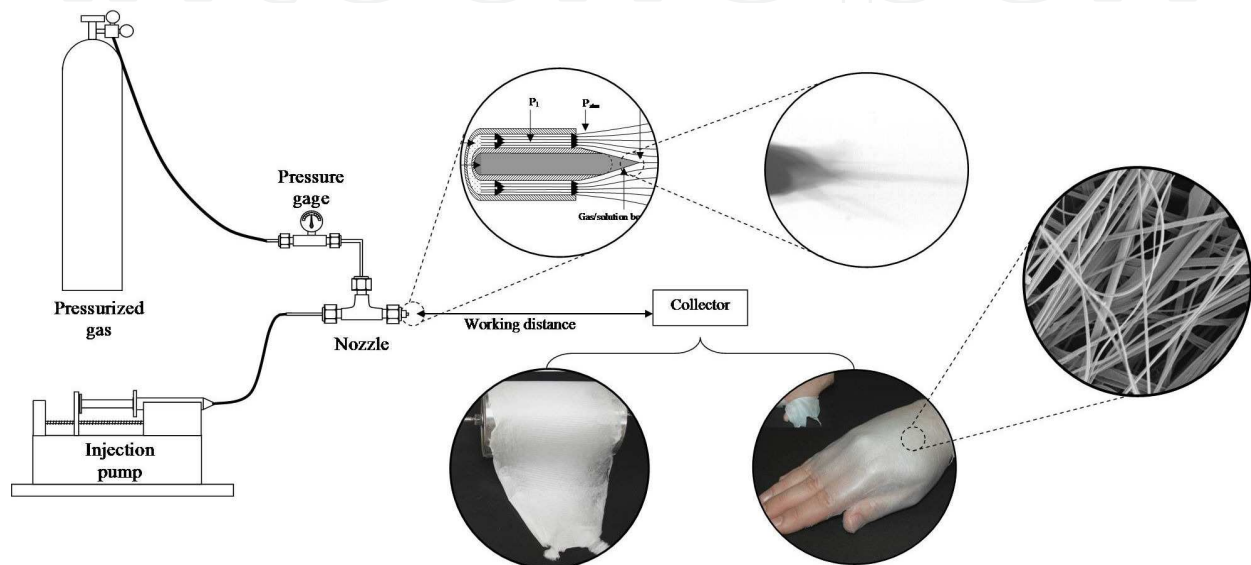


Fig. 10. Schematic illustration of the Solution Blow Spinning technique [56].

### 2.3.6 Electrospinning

A very innovative and promising technique to obtain electroactive fibers is through the application of a static electric field on a polymer solution or melt. This technique known as *electrospinning* can be used to produce polymer fibers down to the nanometer. Contrasting with the most common fiber processing techniques as melt spinning, dry spinning, wet spinning and extrusion, electrospinning is able to produce ultrathin fibers with low cost and elevated surface area. This point is of particular interest for producing sensors, actuators and other electroactive devices, especially possible when conducting polymers are used in electrospinning. MacDiarmid and his group firstly verified the possibility to electrospin fibers of conducting polymers once no chain degradation was observed after electrical field application [63, 64]. Since then, many conducting polymers such as polyaniline, polypyrrol and polythiophene have been used to produce nanosized electrospun fibers [65-68]. Although the available literature on electrospinning of polymer mats is extensive, there are still few reports on electrospinning of electroactive polymers and its related applications<sup>1</sup>. Details of the electrospinning process will be given in the next section.

<sup>1</sup> A total of 98 scientific papers and patents were found at SciFinder and 56 at Web of Science until May, 2011 under the key words: "conjugated polymer electrospinning".

### 3. Electrospinning process

#### 3.1 Basics of electrospinning

Electrospinning has emerged as an experimental technique based on the application of a static electric field on a polymer solution or melt through a spinneret. The electrostatic spinning of polymer fibers matches both basic science and technological development pointing the development of new materials with unrelated properties that will cause revolution in the way of producing polymer materials [2].

On a first approach, electrospinning appears to be a simple and easily controllable technique able to produce polymeric nanofibers. A typical experimental setup is based on a capillary injection tip, a high voltage source able to apply electric fields of  $100\text{--}500\text{ KVm}^{-1}$  and a metallic collector, or counter-electrode. Electric current in electrospinning experiments are usually in the order of few miliamperes [2]. A typical apparatus for electrospinning of polymers consists of an injection pump with hypodermic syringe to pump solution through the needle/nozzle, a grounded collector that can be either stationary or rotating, and a high voltage supply. Experiments can also be carried out in a box in order to precisely control environmental conditions such as temperature and relative humidity (see Figure 11).

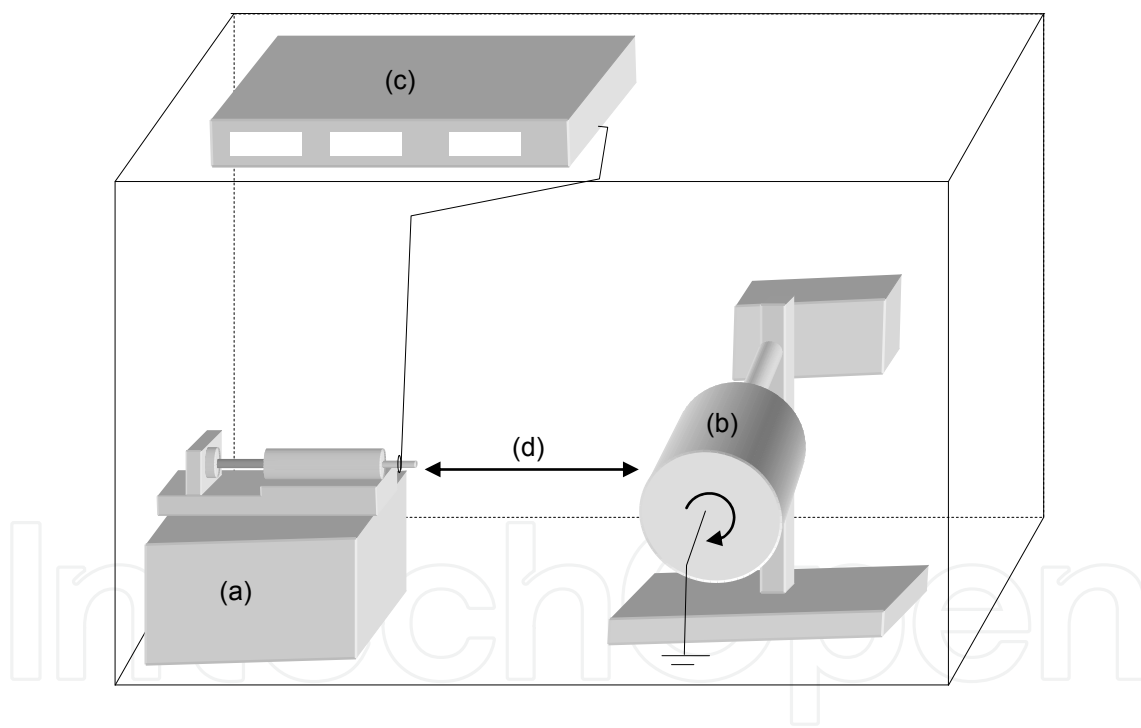


Fig. 11. A typical setup used to produce nanofibers by electrospinning. (a) Injection pump with hypodermic syringe; (b) grounded collector; (c) high voltage supply; and (d) working distance.

The electric potential causes the deformation of the fluid drop and, when the applied voltage develops enough force and balances with the fluid surface tension of the polymer solution, the drop is deformed under a cone shape with a semi-vertical angle of approximately  $30^\circ$ . Recently, Reneker and coworkers [69] demonstrated that beyond this critical value (Rayleigh limit), the electrostatic forces generated by the charge carriers present in fluid (which move toward the surface of the polymer solution) overcome the surface

tension and the deformed droplet undergoes to a transition zone just before the fiber jet is initiated to the collector screen [69-72]. At this moment, fluid is submitted to an expressive stretching, but inside tension is still small and the authors proposed a Newtonian flux behavior in this transition zone. Experimental measurements have shown that typical stretching rates in transition zone are around  $100 - 1000 \text{ s}^{-1}$  [69]. Thus, any change in jet format will imply a dynamic redistribution of charges on its surface, leading to instability due to bending caused by this redistribution of electric charges. After, a linear segment takes place and the pre-stretched jet is submitted to rates of  $20 \text{ s}^{-1}$ . In linear segment, the flow is basically controlled by effects of electrical field and the longitudinal tension of the viscoelastic fluid. Due to the high electric fields commonly used in electrospinning, fluid jet is kept stable under small distances (around 2-4 cm) before reach the scattering region, where longitudinal instabilities take place [73-77]. Polymer jets can be ejected at velocities up to  $40 \text{ m.s}^{-1}$  [2], Figure 12 represents the different regions of a polymer jet in electrospinning process.

A closer look to the electrospinning process reveals its intricate complexity. Recent studies compare the electrical instability on electrospinning process to aerodynamic instabilities [77] where partial differential equations of the aerodynamics of the fluid jet with electric field equations are used to detailed describe the phenomenon [78,77,79]. Many theoretical models have been used to describe the combination of a viscoelastic fluid driven by an electrical field.

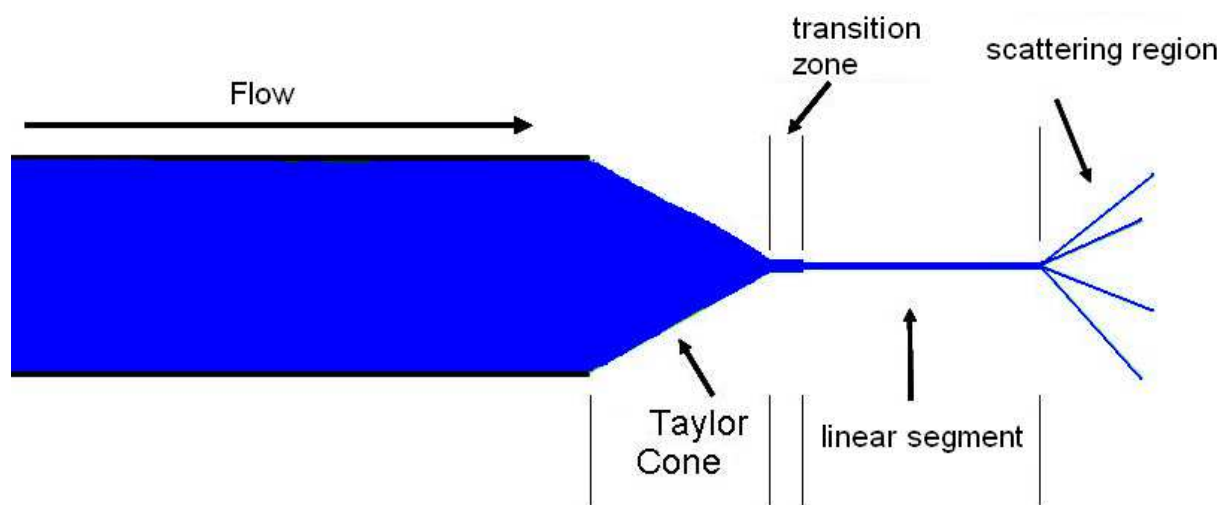


Fig. 12. Representation of fluid deformation in electrospinning process.

Based on Taylor studies and with the use of high velocity cameras, Baumgarten proposed that the electrospinning process occurs in two moments: (1) geometry deformation of the fluid droplet by the electric field and (2) the formation of a continuous jet from the top of deformed droplet [80]. A one dimensional model was proposed by Hohman e Gañán based on numerical calculations of fluid atomization in a steady state. Based on this approach, the authors were able to reasonably describe the intermediate region between the cone and scattering region of electrified jets [81,82]. Later, Holman and coworkers studied the fluid jet stability under an electric field [70, 83]. The studies searched for evidences of the experimental parameters on the beginning of electrospinning process. The authors proposed

that the nanofiber formation is governed by the scattering region, where the surface of charged jets interacts to the electric field leading to the scattering region (Figure 9). Many others theoretical models have been proposed to electrospinning. Recently, Doshi and Reneker considered the electrospinning jet as a mass-spring system divided into four distinct regions containing beads of electrical charge ( $e$ ) and mass ( $m$ ) connected by viscoelastic elements [71,85-87].

For many applications a precise diameter control is required. Fiber dimensions and morphology depend strongly on process parameters as, for example, polymer properties: molar mass, molar mass distribution, glass transition temperature, solubility; solution properties as viscosity, viscoelasticity, concentration, surface tension, electrical conductivity, dielectric constant, vapor pressure and ambient conditions as humidity and temperature. Basically, electrospinning process parameters can be classified into three different topics; solution parameters, process parameters and ambient parameters.

Solution parameters as viscosity, electrical conductivity, and surface tension affect directly the fiber dimensions and morphology. Viscosity is one of the most important solution parameters. Beadless fibers are commonly obtained when the polymer solution develops a minimum polymeric chain network, the entanglement concentration. In fact, both solution viscosity and concentration are related by Berry Number ( $Be$ ). Experimental findings show that the diameter of electrospun fibers is dependent of solution concentration and polymer chain conformation in solution. Thus, the Berry Number is defined by equation 1;

$$Be = [\eta] * C \quad (1)$$

where,  $[\eta]$  is intrinsic polymer viscosity and  $C$  is the polymer solution concentration. As the degree of polymer chain entanglements can be represented by the  $Be$  number, one can say that  $Be$  values determines the electrospun fiber diameter. When  $Be < 1$ , polymer molecules in solution are sparsely distributed and there is a low probability of an individual molecule to bind with another. As a result, only beads and beaded fibers are formed. Figure 13, compares typically beaded and beadless fibers.

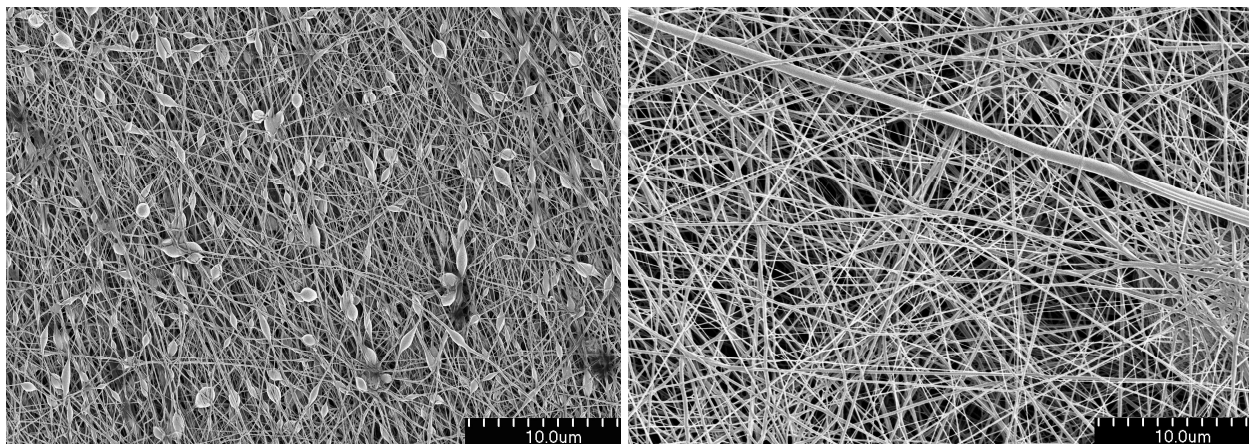


Fig. 13. (a) Poly(lactic acid) electrospun fibers with beaded morphology, (b) beadless Poly(lactic acid) electrospun fibers.

At  $1 \leq Be \leq 2.7$ , entanglement probability increases and favorable conditions for fiber production takes place. This  $Be$  number range is convenient for nanofiber production. At  $Be$

$\geq 2.7$ , polymer chain entanglements probability increases and the average fiber diameter goes above the micrometer range [88, 89].

Surface tension is directly related to the Taylor cone formation and this is related to the electric field strength applied over the fluid droplet able to deform its shape. This tension value is called critical tension and polymer solutions with different solvents will have different the critical values. Also, it was observed that the decrease in surface tension values will favor a beadless morphology [90, 91].

The electrical conductivity of solution also plays an important role on fiber morphology. Higher solution electrical conductivity is associated to a greater number of charges in solution, which favors the electrospinning process. Generally, both electrical conductivity of solvents and polymers are small and in some cases, inorganic salts are added to solution in order to favor the spinning process. This methodology is successfully used in production of nanofibers with uniform diameter values with beadless morphology [92,93]. Moghe and coworkers [94] produced bead-free ultrafine fibers with narrow fiber diameter distribution from poly( $\epsilon$ -caprolactone) (PCL) via electrospinning. The high quality product was achieved with the use of a new solvent system that involves an acid-base reaction to produce weak salt complexes, which serve to increase the conductivity of the polymer solution.

In electrospinning, process parameters are typically considered as the applied electric field, working distance, flow rate and, in some cases, rotor (collector) velocity.

According to Doshi e Reneker [71], there is a range of applied voltage values where a stable jet is obtained for poly(ethylene oxide) solutions. For example, solutions at 6 wt.%, a stable jet is formed between 5 and 15 KV, with a working distance of 12.5 cm. The authors also concluded that the diameter of the jet decreases as it moves away from the needle tip until it reaches a minimum value dependant of the Taylor cone initiated. These values were also corroborated by Medeiros and collaborators for poly(vinyl alcohol) [95]. Also, according to Deitzel and coworkers [96], applied voltage values are directly related to beads formation and the monitoring of electric current during the process is able to indicate the electric field values where beads density significantly increases.

Carroll and Joo [97] reported a study considering axisymmetric instabilities of highly conducting viscoelastic solutions of poly(ethylene oxide). In this theoretical study, a linear stability analysis combined with a model for stable electrospun jet was used to calculate the expected bead grow rate and the wave number for a given electrospinning conditions. According to the authors, the analysis reveals that the unstable axisymmetric mode for electrically driven, highly conducting jets is not a capillary mode, but is mainly driven by electrical forces due to the interaction of charges on the jet. The authors observed that both experiments and stability analysis elucidated that the axisymmetric instability with a high growth rate can be seen in practice when the electrical force is effectively coupled with viscoelastic forces.

Unlike the applied electric field, the working distance, i.e., distance between needle tip and the collector, seems less important in the formation and morphology of fibers. However, a value of minimum working distance is needed to ensure complete solvent evaporation, and a maximum value for the electric field is effective in forming the Taylor cone and consequently the formation of nanofibers [92]. As observed by Gomes and coworkers [93], fiber diameter decreases when the working distance increase from 2 to 14 cm. Further increase in distance, from 14 to 20 cm, has no effect on fiber diameter. Also, in small

working distance condition, solvent is not completely evaporated when fibers reach the collector and porous morphologies are obtained.

The environmental parameters, temperature, humidity and air composition, can affect the formation and morphology of nanofibers [98]. Medeiros and coworkers [99] also found that electrospun fibers of PVA, PLA, PVC and PS had their morphology strongly dependent on the relative humidity surrounding the spinning process. Depending on the relative humidity used, fibers with different sizes and porosities were obtained. With the same aim, Vrieze and coworkers [99] studied the effect of humidity and temperature in the nanofibers of cellulose acetate and PVP (polyvinyl pyrrolidone). They found that for PVP increased humidity resulted in a decrease in the average fiber diameter, while for cellulose acetate fiber diameter increased. The authors attributed this behavior to the chemical nature of the polymer. However, the dependence of the diameter with temperature was not linear for both polymers, since for lower temperatures, 283 and 293K, initially there was an increase in diameter and with increasing temperature, 303K, there was a decrease in diameter [99].

Chuangchote and coworkers [100] promoted an extensive study on the effect of different solvents on the electrospinnability of PVP fibers. The authors confirmed that dielectric constant, viscosity, and surface tension of the solvents affect the electrospinnability, morphological appearance, and fiber size. The authors also observed that small and uniform PVP fibers can be obtained using solvents with high dielectric constants, low surface tension, and low viscosity. Furthermore, diameters of PVP fibers decreased with the dielectric constant, dipole moment, and density of the solvents.

### 3.2 Processing parameters of electroactive polymers

Electroactive polymers have a very specific chemistry which may limit the obtention of purely conjugated polymers. Because of limitations on molecular weight and solvents suitable for electrospinning, only a few conjugated polymers such as polyaniline, poly(dodecylthiophene), and poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] have been electrospun [101]. Thus, electrospinning of conjugated polymers is very limited due to the absence of chain entanglement (conjugated backbones are stiffer and offer low or almost no entanglements), which is considered a prerequisite in electrospinning technique.

Some authors have proposed several modified process approaches to obtain electroactive electrospun nanofibers [102]. One first practical and easy way is to spin a nonconductive polymeric web and after, polymerize conductive polymers onto fiber surface. For example, conductive Polyamide-6 (PA-6) nanofibers were prepared by polymerizing pyrrole molecules directly on the fiber surface of PA-6. Firstly, a solution of PA-6 added with ferric chloride in formic acid was electrospun with average diameter values around 260 nm. Secondly, fibers were then exposed to pyrrole vapor and a compact coating of polypyrrole was formed on the fiber surface. According to the authors, polypyrrole coating on the fibers turned out to be conductive with a pure resistive characteristic [102].

A similar approach was used by Ketpang and Park [103] to electrospin PVDF/PPy composites which were prepared by spinning a nonwoven web from a solution of PVDF and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in DMAc and then exposing the spun fibers to pyrrole vapors in order to produce the conductive composites. According to authors, the electrical conductivity of the PPy composites was affected by the fabrication method and oxidant content in the non-woven web.

Lee and coworkers [104], produced uniform poly(3-hexylthiophene), P3HT nanofibers by electrospinning. As the solubility of P3HT is limited in chloroform the authors adapted the nozzle for being clogged by using a coaxial electrospinning setup where polymer solution is fed through the inner nozzle and pure chloroform is provided through the outer nozzle in order to retard solvent evaporation. According to the authors, this continuous method can be employed to produce organic-based devices on a massive scale.

A very interesting adaptation on electrospinning methodology was developed by Sundarrajan and coworkers for producing a P3HT/PCBM electroactive solar cloth [105]. As noted by the authors, electrospinning of pure conjugated polymers is not possible due to the absence of polymer chain entanglements. Since, they proposed the co-electrospinning of poly(3-hexyl thiophene) (P3HT) (a conducting polymer) or P3HT/PCBM as the core and poly(vinyl pyrrolidone) (PVP) as the shell. This approach revealed successful once the PVP shell could be washed giving rise to conductive P3HT or P3HT/PCBM cloth.

On the other hand, MacDiarmid's group was the first to report the production of pure polyaniline (PAni) fibers by electrospinning [63]. According to the authors, 100% PAni fibers with average diameter of 139 nm and conductivity value of a single fiber  $\sim 0.1$  S/cm were produced placing a 20 -wt% solution of polyaniline in a 98% sulfuric acid in a glass pipette above a copper cathode immersed in pure water at 5000 V potential difference. Later, Chronakis and coworkers produced pure PPy electrospun fibers with diameters of  $\sim 70$  nm by dissolving  $[(PPy_3)^+(DEHS)^-]_x$  in DMF, where the doping agent (DEHS)<sup>-</sup> derives from di(2-ethylhexyl) sulfosuccinate sodium salt (NaDEHS) [106].

In order to improve polyaniline processability, a first approach to obtain PAni.HCSA doped nanofibers blended with usual polymers by electrospinning was done by MacDiarmid's group [64]. In this study a non-woven mat was obtained by using a polyaniline/polyethylene oxide PEO solution dissolved in chloroform. By controlling the ratio of polyaniline to PEO in the blend, fibers with conductivity values comparable to that of PAn.HCSA/PEO cast films were produced.

Another study on production of PAni(CSA) nanofibers dispersed in poly(methyl methacrylate) (PMMA) solution in chloroform were produced by Veluru and coworkers [107]. According to the authors very good aligned fibers with diameters in the range of 500nm to 5 $\mu$ m were obtained and dc conductivity was estimated to be around 0.28 S/m.

Gizdavic-Nikolaidis and coworkers [108] used a mixture of dimethyl sulfoxide/tetrahydrofuran in order to obtain homogeneous blended nanofibers of HCl-doped poly(aniline-co-3-aminobenzoic acid) (3ABAPANI) copolymer and poly(lactic acid) (PLA) for tissue engineering. Once solvent system DMSO/THF (50:50) is quite difficult to be removed from the nonwoven mats, the authors used a heated collector to facilitate the solvent removal. This procedure can be considered essential in cases where nonwoven fiber mats will be used in cell growth. Besides composite electroactive fibers achieve lower conductivity values comparing to pure conjugated polymer fibers, this lower conductivity is quite appropriate to tissue engineering.

As observed earlier, the addition of ions in electrospinning solution can improve fiber spinnability due to the increase of charge carriers in solution. It is also known that conjugated polymers may have high density of charge carriers and this can also affect the electrospinning process. It was recently observed that the addition of PAni.TSA to PLA solution in HFP caused similar effect of inorganic salts addition [65]. According to the authors, the average fiber diameter reduced around 400 nm after addition of 0.2 -wt% of

PAni.TSA. Also, diameter distribution narrowed and a beadless morphology was observed. Furthermore, electrorheological effects can be observed in polymer solution with high density of charge carriers [66].

Composite nanofibers of Poly(vinylidene fluoride-trifluoroethylene)/polyaniline-polystyrene sulfonic acid with diameters of  $\sim 6$  nm were reported by Abreu and coworkers [109]. As observed before, the addition of the conjugated polymer PANi-PSSA also increased the charge density of the solution and assisted the fabrication of homogeneous nanofibers at lower than normal PVDF concentrations in DMF.

Attout and coworkers used a very interesting experimental setup to produce aligned polyaniline based nanowires and nanotubes based on electrostatic steering [110]. As demonstrated by the authors, electrospun nanofibers can be aligned on a substrate using an alternative electrostatic field generated between two collectors. This technique suggests promising strategies to achieve fiber alignment and counting with an "immobile" experimental setup.

### 3.3 Electrospun electroactive polymer fibers: novel properties due to the size reduction, uses and devices

Nanofibers of electroactive polymers have received great attention recently because of their unique and useful properties [63]. New and unrelated properties may arise from size confinement which may be important for several applications in electronic devices, optics and biomedical materials [111-113], protective clothing [114], filtration media [115], charge storage devices [116,117], sensors and actuators [118-120].

Recently Shin and coworkers fabricated conducting nanofibers by blending multiwalled carbon nanotubes (MWNTs) and polyaniline (PAni)/poly(ethylene oxide) (PEO) using electrospinning. The authors observed an unexpected transition in the electrical conductivity of the conducting composite while measuring the  $I-V$  characteristics of the nanofibers aligned on an electrode when they were exposed to an applied high voltage. This unexpected transition in the electrical conductivity was attributed to the interactions between the MWNTs and the conducting polymer inside the fiber due to an annealing effect of the PANi/PEO matrix from the thermal dissipation of the CNTs. The authors also related this unusual transition to the self-heating effect of the MWNTs incorporated into the conducting polymer which will be very helpful in enhancing the electrical properties of nanoscale conducting composite fibers [121].

Jeong and coworkers [122] prepared a conductive composite based on multiwall carbon nanotubes and nylon 6,6 by electrospinning. In this work a methodology was developed in order to produce stable dispersions of MWNT's functionalized with  $-NH_2$  terminations in formic acid. After, nylon 6,6 solution in formic acid was electrospun with different filler concentration. According to the authors, the  $I-V$  characteristics were found to be non-ohmic and improved with increasing filler concentration in the nylon nanofiber. This increase was attributed by the authors to the enhancement of the electron conduction process by the increase of MWNT content.

Babel and coworkers electrospun nanofibers of two series of binary blends of poly[2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV) with regioregular poly(3-hexylthiophene) (PHT) and (MEH-PPV) with poly(9,9-dioctylfluorene) (PFO) aiming the production of fibers with tunable, composition dependent, optical, and charge transport properties that could be exploited in nanoscale devices. The authors were able to produce



fibers with diameters ranging from 100 to 500 nm. It was observed phase-separated morphology by SEM images. However, because of confinement of the liquid jets during electrospinning, the length scales of the phase separation in these blend fibers are much smaller than those of the MEH-PPV/PHT blend thin films prepared by spin coating where the length scales of the phase-separated domains were on the order of 100-150 nm [100]. Furthermore, the red shift in electronic absorption peaks suggests that the polymer chains in the fibers are more extended, which may lead to the increase of  $\pi$ -conjugation length. Moreover, the extended polymer chains should be oriented along the fiber axis due to the strong stretching of the liquid jet during electrospinning better  $\pi$ -electron delocalization. An interesting feature in the absorption spectra of MEH-PPV/PFO blend nanofibers is a 20- 30 nm red shift of the PFO absorption band to 400- 410 nm, suggesting that the PFO chains are also extended and oriented along the fiber axis.

PAni.TSA/PLA blended electrospun nanofibers have been recently produced [67]. The authors observed no phase segregation of PAni in PLA matrix in electrospun fibers while phase segregation was observed in cast films with the same composition. According to the obtained results, the authors concluded that due to rapid solvent evaporation in electrospinning process, no crystalline structures in fiber mats were formed compared to cast films. Highly homogeneous electroactive fibers can be useful in construction of electronic devices and sensors. Similar behavior was observed to the (PVDF-TrFE/PANi-PSSA) electrospun nanofibers [123].

Laforgue reported the production of flexible supercapacitors using electroactive fibers obtained by electrospinning [124]. In this work the author demonstrated that Polyvinylpyrrolidone (PVP) fibers covered with poly(3,4-ethylenedioxythiophene) (EDOT) by vapor phase polymerization. The conductive mats presented elevated electrical conductivity ( $60 \pm 10 \text{ S cm}^{-1}$ ) and were separated by a layer of PAN in order to assembly an all flexible capacitor device.

According to the authors, the electrochemical performances of the solid-state supercapacitors were very similar to the ones obtained in liquid electrolyte. Owing to the nanostructure nature of the active materials, an effective wettability by the electrolyte and a limited diffusion length of the doping ions within the polymer structure were observed [124].

A similar approach was used by Sundarrajan and coworkers to produce a solar cloth by electrospinning technique as presented previously in this chapter [105]. The authors have found an efficiency of fiber cloth around  $8.7 \times 10^{-8}$ , however environmental parameters and fiber diameter reduction can be improved in order to produce more efficient materials.

Electrospun conducting fibers are also used in production of biocompatible systems for tissue engineering and biosensors. Lee and coworkers produced PLGA electrospun nanofibers coated with polypyrrole for neural tissue applications [125]. The authors used PPy-PLGA electrospun meshes to support the growth and differentiation of rat pheochromocytoma 12 (PC12) cells and hippocampal neurons comparing to non-coated PLGA meshes. It was suggested that PPy-PLGA may be suitable as conductive nanofibers for neuronal tissue scaffolds.

Also, conductive polymers can be blended with other polymers to provide an electrical current to increase cell attachment, proliferation, and migration. McKeon and coworkers [126] electrospun several polyaniline and poly(D,L-lactide) (PAni/PDLA) mixtures at different weight percents. Interestingly only the 75/25 electrospun scaffold was able to

conduct a current of 5 mA with a calculated electrical conductivity of  $0.0437 \text{ S cm}^{-1}$ . Later, primary rat muscle cells were cultured on scaffolds and on tissue culture polystyrene as a positive control. The authors observed that, although the scaffolds degraded during this process, cells were still able to attach and proliferate on each of the different scaffolds. The cellular proliferation measurements showed no significant difference between the four groups measured and the conductivity and cellular behavior demonstrate the feasibility of fabricating a biocompatible, biodegradable, and electrically conductive PDLA/PANi scaffold.

As cited before, HCl-doped poly(aniline-co-3-aminobenzoic acid) (3ABAPANI) copolymer and poly(lactic acid) (PLA) blend were electrospun in the form of three-dimensional networks with a high degree of connectivity, onto glass substrates [108]. The authors evaluated the ability to promote proliferation of COS-1 fibroblast cells over this conductive scaffold. According to the authors, this new class of nanofibrous blends can potentially be used as tissue engineering scaffolds and showed promise as the basis of a new generation of functional wound dressings that may eliminate deficiencies of currently available antimicrobial dressings.

Li and coworkers investigated the potential applications of polyaniline containing gelatin nanofibers for producing conductive scaffolds for tissue engineering purposes [127]. The authors have found that the polyaniline addition affects the physicochemistry of PANi-gelatin blend fibers and that this kind of substrate is biocompatible and support the cells (H9c2 rat cardiac myoblast) attachment, proliferation and growth. Similar work was developed by Borriello and coworkers on testing PANi and polycaprolactone (PCL) electrospun membranes as platforms for to mimic either the morphological and functional features of the cardiac muscle tissue regeneration [128]. The authors observed that development of PANi/PCL membranes by electrospinning with controlled texture can create an electrically conductive environment and this environment can stimulate the cell differentiation to cardiomyocytes, and can successful be used in the myocardium muscle regeneration.

Aussawasathien and coworkers produced composite fibers of Poly(o-anisidine)-polystyrene via electrospinning for chemical vapor sensing [129]. Sensibility of the composite fibers were tested under water and ethanol vapor (being that) the sensors elements responded better to the high polarity of the solvent. The CSA doped POA/PS composition seems to be stable under the submitted ambient one to ethanol. The sensor could be reused several times without any change in sensing behavior and/or damage to the sensing materials.

A flexible nanotube membrane of Poly(3,4-ethylenedioxythiophene) (PEDOT) was produced by Kwon and coworkers electrospinning mediated for ammonia gas detection [130]. Initially, Poly(vinyl alcohol) (PVA) solution was electrospun and further treated with  $\text{FeCl}_3$  solution to adsorb Fe ions on the nanofibers surface. Later, EDOT monomer was evaporated and polymerized on the PVA surface leading to coaxial PVA/PEDOT fibers which were after washed with distilled water giving 140 nm PEDOT tubes. According to the authors, PEDOT nanotubes achieved electrical conductivity values of  $61 \text{ S cm}^{-1}$ , higher than the usual PEDOT nanomaterials produced with  $\text{FeCl}_3$ . PEDOT nanotubes revealed owing faster recovery times than PVA/PEDOT coaxial fibers due to the elevated surface area, demonstrating the possibility of this methodology to produce 1D nanomaterials for sensors applications.

Pinto and coworkers evaluated the electric response of isolated polyaniline fibers to vapors of aliphatic alcohols [131]. According to the authors, the large surface to volume ratio, the uniform diameter and small quantity of active material used in the sensor construction are comparable to or faster than those prepared from nanofiber mats of the same polymer. Also, the sensors made from individual fibers exhibit larger responses, especially for bigger alcohol molecules, and also show true saturation upon exposure and removal of the alcohol vapor. As observed by the authors, the response of sensors made from electrospun nanofibers to small alcohol molecules is opposite to that observed for nanofiber mats. This effect was related by the authors to the doping process used in the preparation of the polymer in either case [135].

#### 4. Conclusions and perspectives

Nanotechnology has recently emerged as a unique and fruitful area in modern science that basically encompasses all aspects of the human knowledge. Nevertheless, the use of nanostructured materials dates back to ancient Rome, where artifacts such as wine glasses that changed their color according to the incidence of light were made with gold nanoparticles. Obviously, the knowledge about atomic and molecular manipulation did not exist in those ancient times and only recently with the perception of Richard Feynman and the work of many scientists, nanotechnology has become such a broad field of science with enormous implications and advancements. In fact, emergence of nanotechnology began in the 1980's caused by the convergence of experimental advances such as the development of the scanning tunneling microscope in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory, and the discovery of fullerenes in 1985 by Harry Kroto, Richard Smalley, and Robert Curl, and others discoveries of materials and techniques. Furthermore, the elucidation and popularization of the conceptual framework of nanotechnology began in 1986 with the publication of the book "Engines of Creation: The Coming Era of Nanotechnology" by K. Eric Drexler.

One of the greatest objectives in current research in nanotechnology is based on observations that a number of physical phenomena may become more pronounced as the size of the system decreases. These effects are more significant in case of statistical mechanics and quantum effects usually, especially in case of electronic and optical properties of some solids. Quantum effects become more pronounced, for example, when the nanometer size range is reached, typically at distances of 100 nanometers or less. Another important effect when dealing with nanosized materials is the increase in surface area to volume ratio which is able to produce significant changes in mechanical, thermal and catalytic properties of many materials, including polymers and polymer composites.

Various effects can be considered regarding to the research in nanoscience and nanotechnology of electroactive polymers, especially with regard to electronic conduction in disordered materials of low-dimensional conductors and also with respect to the significant increase in surface area. The latter is considered of especial interest in research and development of sensors based on electroactive polymers.

Electrospinning technique allows us to obtain electroactive polymeric structures of high surface area and organization at the nanoscale. As we have seen before, electrospinning is easy to operate, relatively low cost, and is capable to produce a wide range of electroactive polymer nanofibers and nanomats that can be uses in many applications, ranging from sensors and actuators to solar clothes, supercapacitors and bioactive materials. However,

there is only a limited number of papers published in this field and there is still need for further investigations, particularly with the regard to understanding the electrospinning process within a single theoretical framework, capable of accurately predict fiber dimensions and morphologies experimentally obtained. This point can be considered of fundamental importance for the development of electrospinning and its applications at larger scales.

In fact, this is a topic that deserves most attention from researchers in electrospinning. Despite the ease of obtaining and operating, fibers productivity by electrospinning is considered very small when compared with other techniques for producing fibers. In this regard, considerable efforts should be made to increase the productivity of spun fibers while precisely controlling dimensions and morphology of the fibers. Some efforts have already been done towards this direction indeed since the time of Formhals, but to date there are no records of large-scale production of electroactive polymer fibers by electrospinning despite the fact that this technique has given its first steps towards mass production of micro and nanofibrous mats. In addition, the emergence of new effects and phenomena related to electronic and ionic transport in conductive nanofibers can be studied in depth which certainly will lead to materials and devices with unknown properties.

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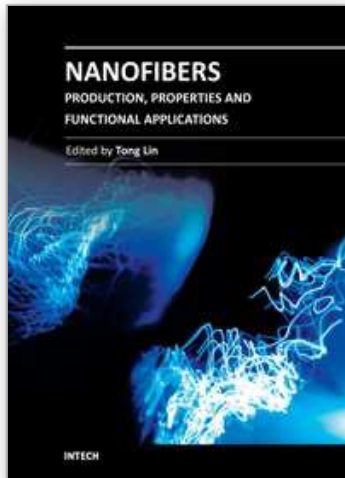
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## **Nanofibers - Production, Properties and Functional Applications**

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As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with a number of novel properties for advanced applications. This book is a compilation of contributions made by experts who specialize in nanofibers. It provides an up-to-date coverage of in nanofiber preparation, properties and functional applications. I am deeply appreciative of all the authors and have no doubt that their contribution will be a useful resource for anyone associated with the discipline of nanofibers.

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