We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Spectroscopy of Polyaniline Nanofibers

Gustavo M. Do Nascimento
Universidade Federal de Minas Gerais
Brazil

1. Introduction

1.1 Synthetic metals

The first materials, synthesized during the 60s, which have found values of conductivity above 1 Scm^{-1}, are called Krogman salts. These salts are square planar complexes of PtX$_4$ or IrX$_4$ (X = CN-or C$_2$O$_4$$^{-2}$), forming structures of chains, which conductivity reaches metallic values when exposed to oxidizing Br$_2$ vapors (Liepins & Ku, 1987). The oxidation of molecular chains causes a reduction of the distances between the atoms of the metals, allowing the filling of the conduction band formed by 5-D$_{ZZ}$ orbitals of neighboring metal atoms in the chain. As a result, the conductivi3ty reaches values as higher as 10^{-7} to 10^{-2} Scm^{-1}, an increase of 10^5 times. Charge-transfer complex forms the second class of molecular substances that have shown high electrical conductivity. Tetrathiofulvalene (TTF) and Tetracyanoquinodimethane (TCNQ) and its derivatives are the most known complex transfers systems (Liepins & Ku, 1987).

The intrinsically conducting polymers (ICPs), more commonly known as "synthetic metals", forms the third class of molecular conductors. Initially, the study of conjugated polymers was hampered owing to their insolubility, infusibility and instability in the air. In the 70s, (Shirakawa & Ikeda, 1974; Shirakawa & Ikeda, 1971) synthesized more stable films of semiconducting poly(acetylene). However, just in 1977, (Chiang et al., 1977; Chiang et al. 1978; Shirakawa et al. 1977; Shirakawa, 2001; MacDiarmid, 2001) found that, when the poly(acetylene) is doped with acid (or base) of Lewis, it is possible to increase the conductivity by 13 orders of magnitude. Since this initial discovery, the development of the conducting polymer field has continued to grow up at an accelerated rate.

The concept of doping is unique and has central importance, because it is what differentiates the conducting polymers from all other types of polymers (Heeger, 2001; Nigrey et al. 1979; Han & Elsenbaumer, 1989). During the process of doping, an insulating or semiconducting organic polymer with low conductivity, typically ranging from 10^{-10} to 10^{-5} Scm^{-1}, is converted into a polymer which shows conductivity in a "metallic" regime (ca. 1-10^4 Scm^{-1}). The addition of non-stoichiometric chemical species in quantities commonly low (≤10%), results in dramatic changes in electronic properties, electrical, magnetic, optical and the structural of the polymer. The term is used for conducting polymers in analogy to the process of doping of crystalline inorganic semiconductors. But, it is important to emphasize that the doping of inorganic semiconductors is of the order of ppm and the dopant causes practically no disturbance into the crystalline structure of the inorganic semiconductor. In the case of doping of the organic polymer, the dopant chemically reacts with the chain and causes disturbance in the crystalline structure of the polymer.

Doping is reversible, and the polymer can return to its original state without major changes in its structure. In the doped state, the presence of counter ions stabilizes the doped state. By adjusting the level of doping, it is possible to obtain different values of conductivity, ranging from the state or non-doped insulating state to the highly doped or metallic. The three major classes of conducting polymers (see Fig. 1) can be doped by p (oxidation) or n (reduction) through chemical and/or electrochemical process (Heeger, 2001; Nigery et al. 1979; Han & Elsenbaumer, 1989).
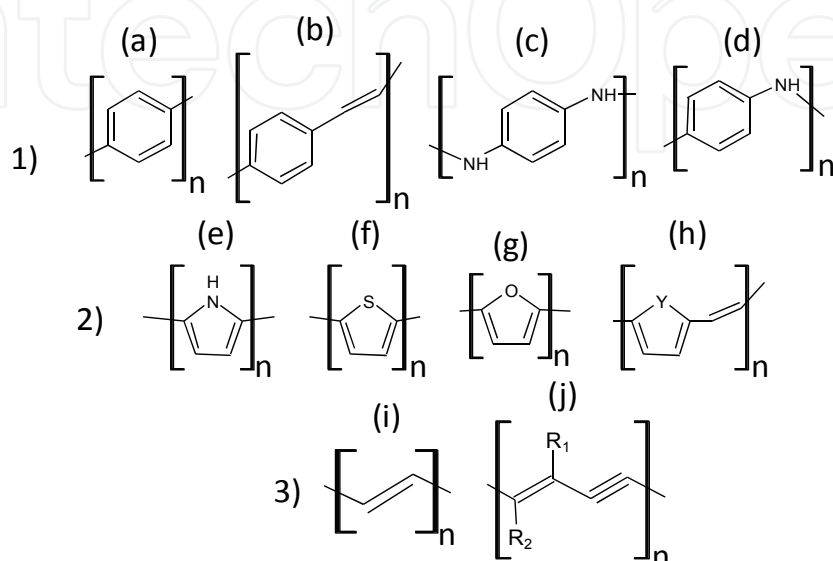

Fig. 1. Chemical representation of the most representative classes of conducting polymers. Group (1) is formed by polymers with benzene ring: (a) poly(*p*-phenylene), (b) poly(*p*-phenylene-vinylene), (c) poly(*p*-phenylenediamine), and (d) poly(aniline). Group (2) is constituted by polymers with cyclopentadiene ring containing a hetero atom: (e) poly(pyrrole), (f) poly(thiophene), (g) poly(furan), and (h) poly(heteroaromatic-vinylene) (where Y = NH, NR, S, O). Finally, the Group (3) is formed by acetylene units, being (i) poly(acetylene) and (j) poly(di-acetylene) (where R_1 and R_2 can be a large variety of organic groups (Song et al., 2004; Asefa et al., 1999; Peng et al., 2005)) the most important ones.

1.2 Polyaniline (PANI)

Polyaniline (PANI) is one of the most important conducting polymers owed to its easy preparation and doping process, environmental stability, and potential use as electrochromic device, as sensor and as corrosion protecting paint. These properties turned PANI attractive to use in solar cells, displays, lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings and sensors. The recent research efforts are to deal with the control and the enhancement of the bulk properties of PANI, mainly by formation of organized PANI chains in blends, composites and nanofibers (MacDiarmid & Epstein, 1989a; MacDiarmid & Epstein, 1989b; MacDiarmid et al. 1987; MacDiarmid & Epstein, 1984). The fully reduced leucoemeraldine base form (LB, see Fig.2 for y = 1) and the fully oxidized pernigraniline base form (PB in Fig.2 for y = 0) are non-conducting forms of PANI. The half-oxidized emeraldine base (EB in Fig.2 for y = 0.5) is a semiconductor but after protonation it becomes a conducting emeraldine salt form of PANI (ES, see structure in Fig. 3) (MacDiarmid & Epstein, 1989a; MacDiarmid & Epstein, 1989b).

EB and ES can also assume two different types of crystalline arrangements depending on the synthetic route used (Pouget et al., 1991; Colomban et al., 1999).

Polyaniline can be synthesized by two main methods, by chemical or by electrochemical polymerization of aniline in acidic media. The chemical oxidation is commonly performed using ammonium persulfate in aqueous acidic media (hydrochloric acid, sulfuric, nitric or perchloric acid) containing aniline. This is the conventional synthetic route of PANI, but one of disadvantages of this route is the presence of excess of oxidant and salts formed during the synthesis, leading to a polymeric sample that is practically insoluble in majority of solvents, making its processing very difficult (Syed & Dineson, 1991).

$$0 \leq y \leq 1$$

y = 1 Leucoemeraldine base

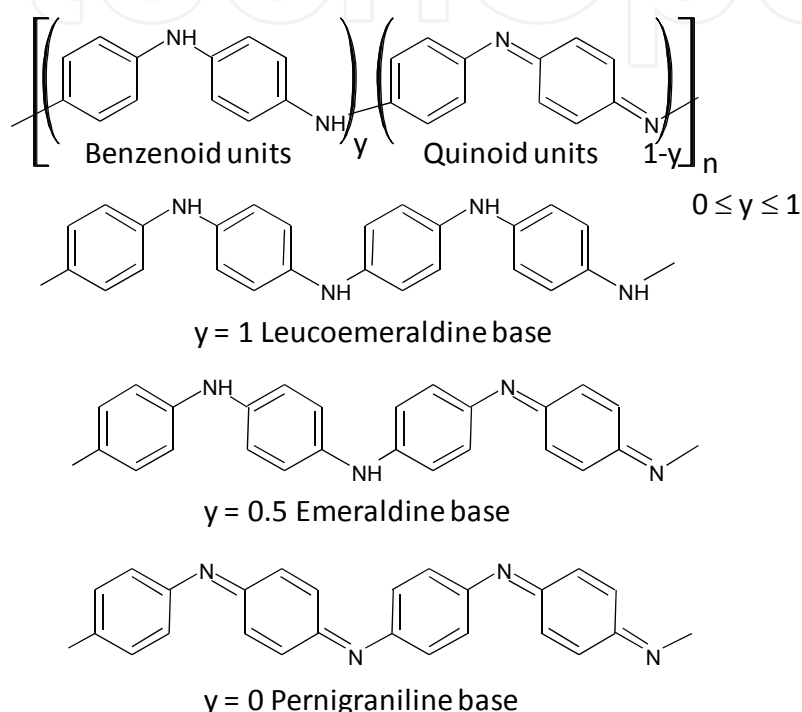y = 0.5 Emeraldine base

y = 0 Pernigraniline base

Fig. 2. Chemical representation of generalized PANI structure and its most common forms.

During the oxidative polymerization of aniline, the solution becomes progressively colored resulting in a solid dark green. The color of the solution is owing to the presence of soluble oligomers formed by coupling of radical cations of aniline. The intensity of the color depends on the environment and also the concentration of oxidant (Syed & Dineson, 1991). There are many variations of the chemical synthesis of PANI, however there is a certain consensus that there are four main parameters that affect the course of the reaction and the nature of final product, being: (1) nature of the synthetic medium, (2) concentration of the oxidant, (3) duration of the reaction, and (4) temperature of the synthetic medium (Syed & Dineson, 1991). The polymerization of aniline was observed as an autocatalytic process (Wei et al., 1989; Sasaki et al., 1986). Kinetic studies suggest that initial oxidation of aniline leads to the formation of dimeric species, such as *p*-amino-biphenyl-amine, N,N'-Biphenyl-hidrazine, and Benzidine (Mohilmer et al., 1962). (Bacon & Adams, 1968) and (Wawzonek & MacIntyre, 1967) showed that the oxidation of aniline and its derivatives in strongly acidic media favor the formation of benzidine, while in a slightly acid or neutral prevails *p*-amino-Biphenyl-amine, but in basic medium the formation of azo bonds, resulting from the head-head coupling is favored, (see Fig. 3). These dimeric species have lower oxidation potential

than aniline and are oxidized immediately after its formation (the N,N'-biphenyl-hidrazine is converted to benzidine through rearrangement that occurs in acid medium (Geniés et al., 1990), resulting two types of charged quinoid-di-imine species. Afterwards, electrophilic attacks in these species, followed by deprotonation, are responsible for the growth of oligomers with subsequent formation of polymer chains of PANI (see Fig. 3).
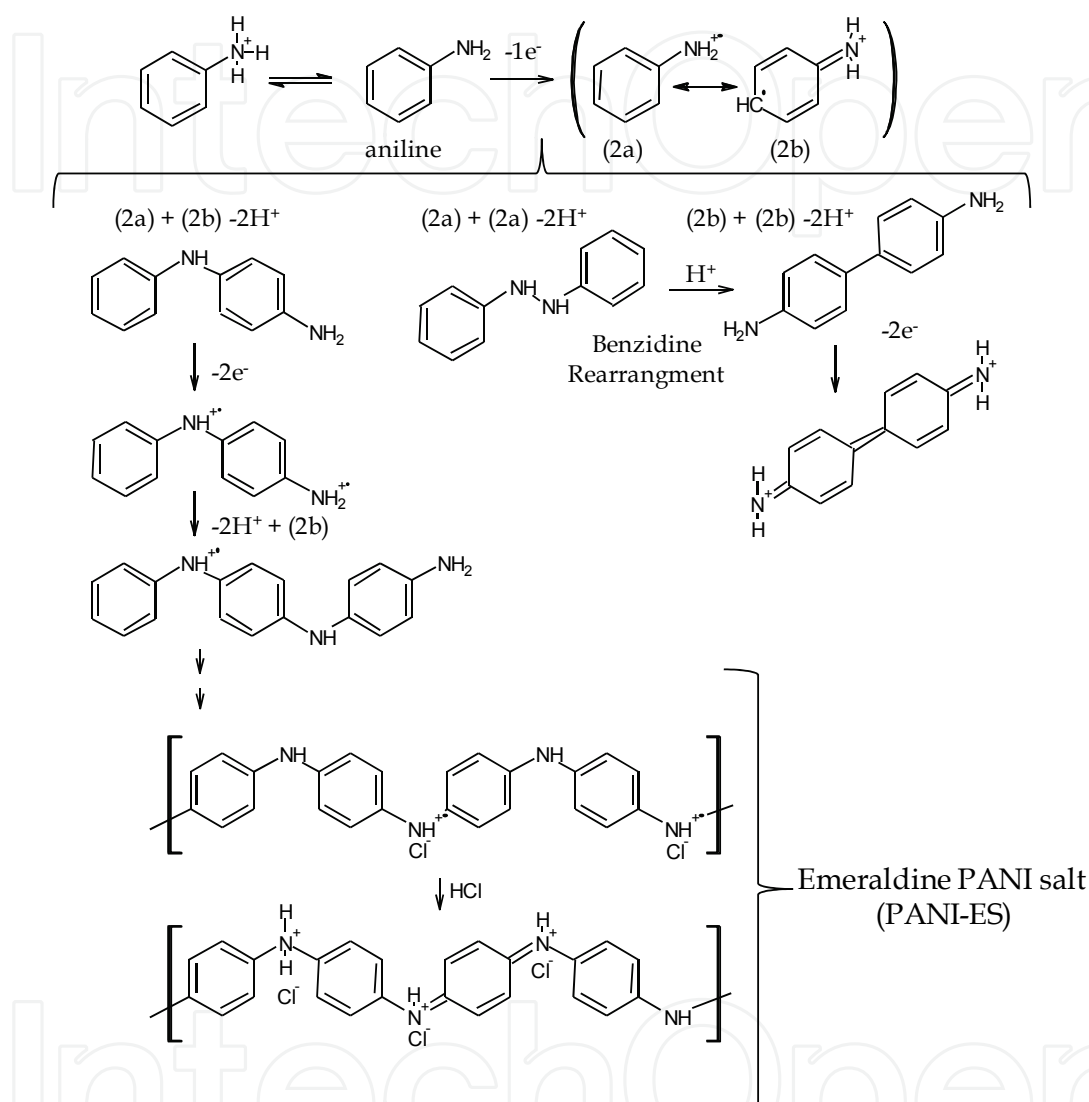

Fig. 3. Schematic representation of the polymerization steps present during the aniline polymerization. The structure of PANI is shown with radical cations (or polarons) and dications (bipolarons) segments.

1.3 Nanostructured polyaniline

The synthesis of nanostructured PANI, especially as nanofibers, can improve its electrical, thermal and mechanical stabilities. These materials can have an important impact for application in electronic devices and molecular sensors owing their extremely high surface area, synthetic versatility and low-cost. The conventional synthesis of polyaniline, based on the oxidative polymerization of aniline in the presence of a strong acid dopant, typically results in an irregular granular morphology that is accompanied by a very small percentage

of nanoscale fibers (Huang & Kaner, 2004a; Huang & Kaner, 2004b). However, different approaches have been developed in order to produce PANI and many other polymers with nanostructured morphology. In this chapter will be analysed the synthetic routes that produce nanostructured PANI, mainly as nanofiber or nanotube morphology, without the use of rigid templates.

The nanostructured PANI has been prepared by different synthetic ways. Nevertheless, these approaches can be grouped into two general synthetic routes, as can be seen in the Fig. 4. Uniform nanofibers of pure metallic PANI (30-120 nm diameter, depending on the dopant) have also been prepared by polymerization at an aqueous-organic interface (Huang & Kaner, 2004a; Huang & Kaner, 2004b). In the first step (see item a) of the interfacial polymerization), the oxidant and monomers (aniline), dissolved in immiscible solvents, are put together without external agitation. Afterwards, some aniline monomers are oxidized in the interfacial region between the two solutions, being formed some oligomers (see item b) of the interfacial polymerization). It is hypothesized that migration of the product into the aqueous phase can suppress uncontrolled polymer growth by isolating the fibers from the excess of reagents. Afterwards, the initial chains grow up and more PANI chains are formed (see step c)). Interfacial polymerization can therefore be regarded as a non-template approach in which high local concentrations of both monomer and dopant anions at the liquid–liquid interface might be expected to promote the formation of monomer-anion (or oligomer-anion) aggregates. These aggregates can act as nucleation sites for polymerization, resulting in powders with fibrillar morphology. It has recently been demonstrated that the addition of certain surfactants to such an interfacial system grants further control over the diameter of the nanofibers. An important part that is frequently neglected or not deeply explained in details is the isolation of the nanostructured PANI from the solution. But, generally, the nanofibers are isolated by filtration in a nanoporous filters, being the isolated polymer washed with different solutions with the aim to clean it up. The solution can be also dialyzed and the cleaned solution containing the nanofibers is centrifuged in order to separate the nanofibers from the solution.

PANI nanofibers or nanotubes can be obtained by making use of large organic acids (see Fig. 4). These acids form micelles upon which aniline is polymerized and doped (see Fig. 4 steps (a), (b) and (c) of micellar polymerization). Fiber diameters are observed to be as low as 30-60 nm and are highly influenced by reagent ratios (Zhang et al., 2002; Qiu et al., 2001; Wei & Wan, 2002; Do Nascimento et al., 2006). Ionic liquids (ILs) have also been used as synthetic media for the preparation of nanostructured conducting polymers (Gao et al., 2004; Rodrigues et al., 2007a; Rodrigues et al., 2007b). Ionic liquids are organic salts with low lattice energies, which results in low melting points and many ILs are liquids at room temperature (Davis Jr et al., 2002). There is a large variety of ionic liquids and the most used ones are derived from imidazolium ring, pyridinium ring, quaternary ammonium and tertiary phosphonium cations. The usual differentiation between conventional molten salts and ionic liquids is based on the melting point. While most molten salts have melting points higher than 200ºC, ionic liquids normally melt below 100ºC (Wasserscheid & Keim, 2000). The most unusual characteristic of these systems is that, although they are liquids, they present features similar to solids, such as structural organization at intermediate distances (Dupont, 2004) and negligible vapor pressure (Earle, 2006). This structural organization can act as a template like system, and PANI nanofibers are obtained when the aniline is polymerized in these media.

Interfacial Polymerization

Polymerization in Micellar media

○ = Oxidant, such as $(NH_4)_2S_2O_8$
● = monomer, such as aniline
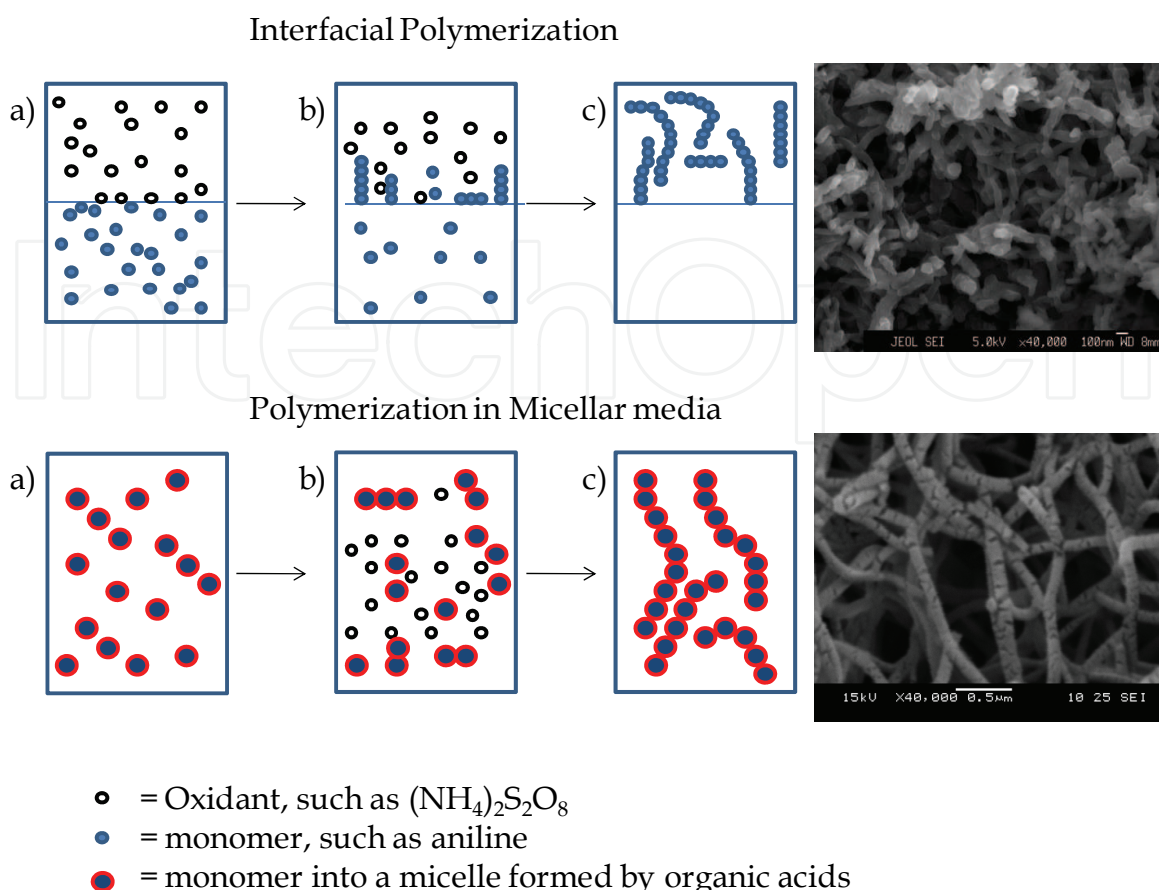◉ = monomer into a micelle formed by organic acids

Fig. 4. Schematic representation of the two polymerization ways that are commonly employed in the preparation of PANI with nanofiber or nanotube morphology. -The interfacial polymerization can be drawn in three steps: a) The top layer is an aqueous solution of 1.0 M HCl acid and ammonium peroxydisulfate (others acids or oxidants can be used); the bottom layer is aniline dissolved in the organic solvent chloroform (others solvents immiscible in water can be used). b) Starting the polymerization and migration of oligomers from organic bottom layer to the aqueous top layer, and c) formation of PANI. The scanning electron microscopic (SEM) image was obtained from the PANI powder obtained from interfacial polymerization using HCl, $(NH_4)_2S_2O_8$, and chloroform. The nanofibers have ca. 30 nm of diameter. The SEM image was obtained from a powdered sample dispersed over a drop of silver glue, and recorded in a Field Emission Gun (SEM, JSM-6330), operated with a high-tension voltage of 5 kV. -The micellar polymerization can be visualized in three steps: a) solubilization of aniline in an aqueous solution containing organic acids that act as surfactants. b) addiction of oxidant and c) polymerization which depending on the concentration of aniline in solution, it is possible to form hollow nanofibers (as named nanotubes) or nanofibers. The SEM image was obtained from the PANI powder obtained from micellar polymerization using β-naphtalenesulfonic acid (β-NSA), $(NH_4)_2S_2O_8$, and molar ratio of β-NSA:aniline of 1:4. The nanofibers have ca. 93 nm of diameter. SEM image was obtained on JEOL low-vacuum SEM (JSM-5900LV operated with 15 kV), with samples covered with 16nm of sputtered gold film.

Thus, the template-free methods, such as interfacial, seeding and micellar can be employed as different "bottom-up" approaches to obtain pure PANI nanofibers. The possibility to

prepare nanostructured PANI by self-assembly with reduced post-synthesis processing warrants further study and application of these materials, especially in the field of electronic nanomaterials. In this chapter this amazing new area of polyaniline nanofibers will be reviewed concerning the state-or-art results of spectroscopic characterization of their structural, electronic and vibrational features. Previous and new results of the spectroscopy of PANI nanofibers, obtained by our group, using Resonance Raman will be considered. Special attention will be given in the correlation of PANI nanofibers morphological stabity and their spectroscopic features. The main goal of this work is to contribute in the rationalization of some important results obtained in the open area of PANI nanofibers.

3. Vibrational spectroscopy of PANI

The resonance Raman spectroscopy (RR), unlike the absorption spectroscopy in the infrared region, uses as radiation source a laser with higher energy (usually light with wavelengths in the visible region of the electromagnetic spectrum) than the corresponding vibrational transitions. However, due to the scattering of the incident light (the Raman process), the vibrational frequencies (Raman bands) can be probed. Generally, the intensities of the Raman bands are linearly proportional to the intensity of the incident light (I_o, see Fig. 4), proportional to the fourth power of the wavelength of the scattered light (λ_s^4 or ν_s in wavenumber units, see Fig. 4), and proportional to the square of the polarizability tensor ($[\alpha]^2$) (Sala, 1995). The situation changes dramatically, when the laser line falls within the region of a permitted electronic transition. The Raman intensities associated with vibrational modes which are tightly coupled or associated with the excited electronic state can suffer a tremendous increase of about 10^5 powers; this is what characterizes the resonance Raman effect. (see Fig. 4). The mathematical and theoretical backgrounds used to the interpretation of the resonance Raman behavior can be found extensively in the literature (Clark & Dines, 1986; Batchelder, 1987; Batchelder, 1984; McHale, 1999). Generally, the tensor of polarizability is described as shown in the Fig.4. The equation is formed in the numerator part by transition dipole moment integrals between the electronic ground state (g, for the vibrational m or n states) and an excited electronic state (e, for any vibrational v states). The sum is done over all possible (e,v) states. In the denominator part is the difference or sum of the scattered and incident light, added by the dumping factor ($i\Gamma_{ev}$) that contents information about the lifetime of the transition states. The theoretical formalism developed by Albrecht et al. commonly employed (Clark & Dines, 1986; Batchelder, 1987; Batchelder, 1984; McHale, 1999). This enormous intensification makes, in principle, the Raman spectrum easy to be acquired. But, in a state of resonance, a lot of radiation is absorbed, leading to a local heating and frequently can be observed a decomposition of the conducting polymer. Despite of this problem, the RR spectroscopy has been largely used in the study of the different chromophoric units present in polyaniline and others conducting polymers, just by tuning an appropriate laser radiation to an electronic transition of the polymer.

In the pioneering work, (Sacricifti & Kusmany, 1987) showed that the intensity of the Raman spectra obtained for the electrochemically prepared PANI at 457.9 nm (E_{laser}= 2.73 eV) is increased when the PANI is reduced (see Fig. 6). The Raman spectrum of PANI in the fully reduced state (applied potential of -100 mV) was identified as being fully formed by benzenoid rings. In contrast, the intensity of the Raman spectra obtained for PANI at 632.8 nm (E_{laser}= 1.97 eV) increased when PANI was oxidized. In the oxidized form (potential
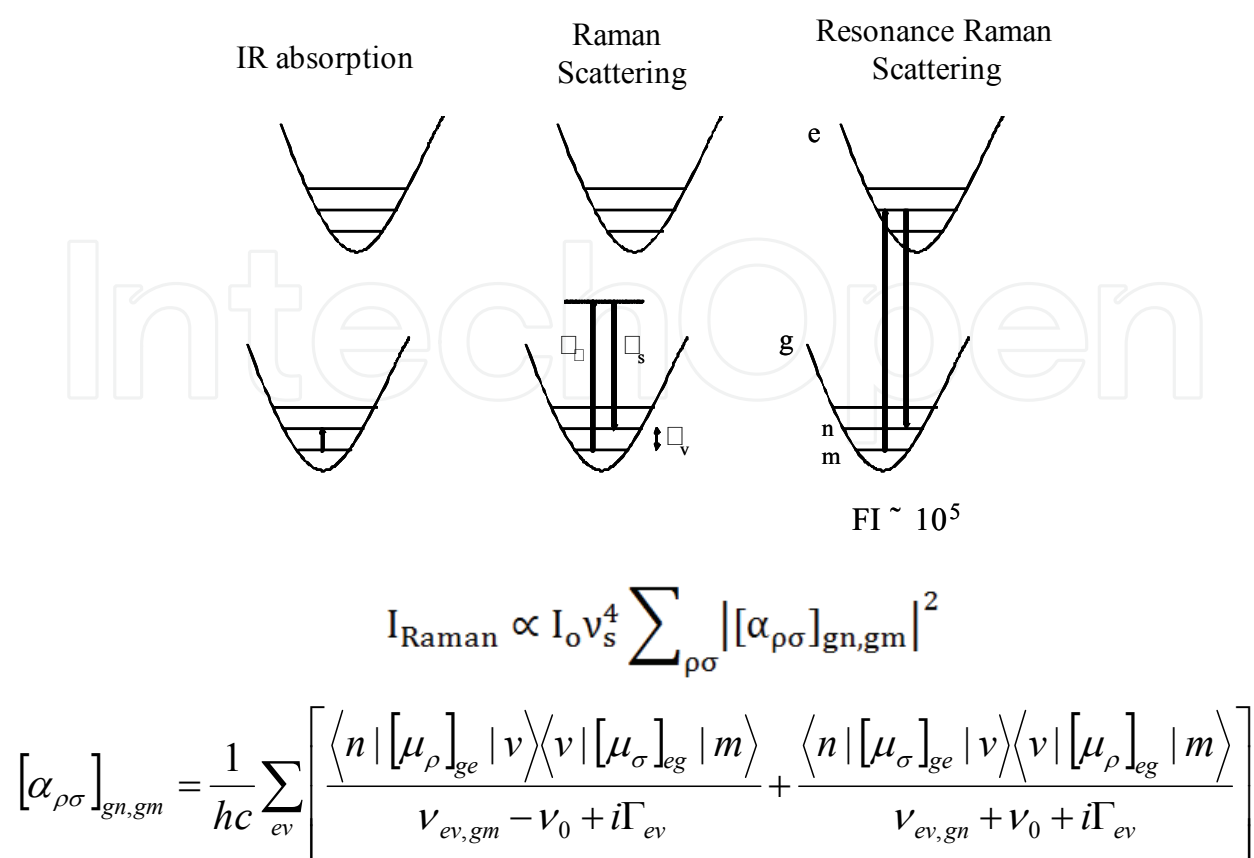
IR absorption   Raman   Resonance Raman
                       Scattering   Scattering

$$\text{FI} \sim 10^5$$

$$I_{\text{Raman}} \propto I_o \nu_s^4 \sum_{\rho\sigma} \left| [\alpha_{\rho\sigma}]_{gn,gm} \right|^2$$

$$[\alpha_{\rho\sigma}]_{gn,gm} = \frac{1}{hc} \sum_{ev} \left[\frac{\langle n | [\mu_\rho]_{ge} | v \rangle \langle v | [\mu_\sigma]_{eg} | m \rangle}{\nu_{ev,gm} - \nu_0 + i\Gamma_{ev}} + \frac{\langle n | [\mu_\sigma]_{ge} | v \rangle \langle v | [\mu_\rho]_{eg} | m \rangle}{\nu_{ev,gn} + \nu_0 + i\Gamma_{ev}} \right]$$

Fig. 5. Schematic representation of two electronic states (ground and excited) and their respective vibrational levels (the electronic and vibrational levels are not in the same scale). The arrows indicated the types of transitions that can be occurred among the different levels. It is important to say that in the case of Raman scattering, if the used laser line (λ_o, or as wavenumber, represent by ν_o) has energy similar to one electronic transition of the molecule, the signal can be intensified by resonance process, know as resonance Raman Effect. In the Figure ν_o and ν_s (the scattered frequency is composed by: $\nu_{ev,gm}$ and $\nu_{ev,gn}$, the stokes and anti-stokes components, respectively) are the laser line and the scattered frequencies, respectively (for illustration purposes, just the Stokes, $\nu_s \langle \nu_o$, component is shown in the diagram). It was given the equations that describe the Raman Intensity and also the tensor of polarizability. The equation is formed in the numerator part by transition dipole moment integrals between the electronic ground state (g, for the vibrational m or n states) and an excited electronic state (e, for any vibrational v states). The sum is done over all possible (e,v) states. In the denominator part is the difference or sum of the scattered and incident light, added by the dumping factor ($i\Gamma_{ev}$) that contents information about the lifetime of the transition states.

applied +600 mV) three Raman bands (1160, 1490 and 1595 cm⁻¹) were identified as characteristics of the quinoid structure of PANI. Another important early work was carried out by (Furukawa et al., 1988; Furukawa et al. 1996). In this work the authors prepared PANI in different oxidation and protonation states and an extensive characterization was realized. Figure 6 presents the segments of PANI and its characteristic Raman bands at their corresponding exciting radiation.
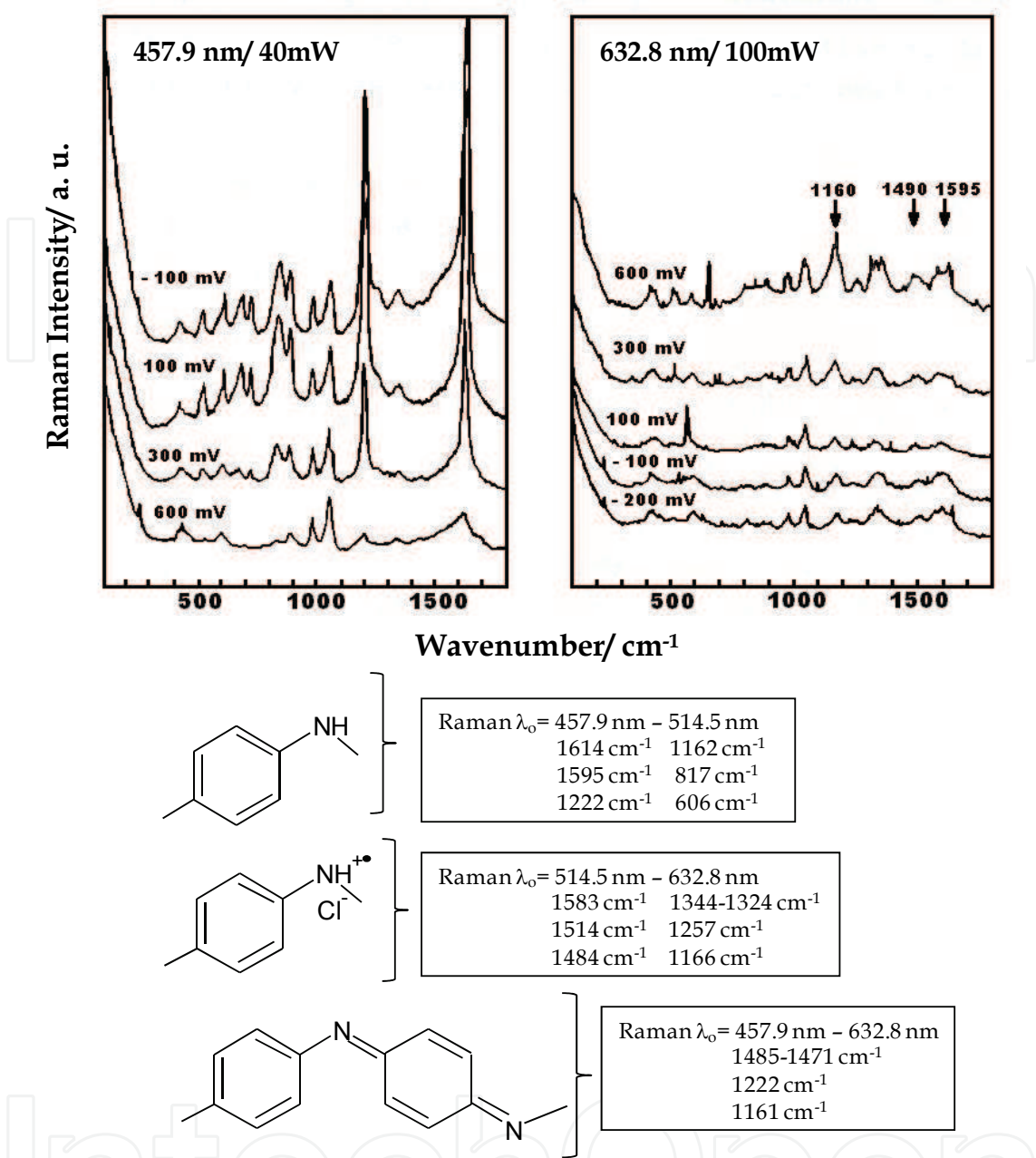
Fig. 6. Top: Raman spectra of PANI in different oxidation stages (the applied voltage is indicated in the figure) at indicated laser line (457.9 nm and 632.8 nm). Reproduction authorized by Elsevier (Sacricifti & Kusmany, 1987). Bellow: schematic representation of segments of PANI and its characteristic Raman bands at indicated laser lines (Furukawa et al., 1988).

(Quillard et al., 1994; Berrada et al. 1995) performed a normal coordinate analysis of PANI in its leucoemeraldine, emeraldine, and pernigraniline base forms. The leucoemeraldine base is characterized by the vibrational modes of the benzene ring in 1618 and 1181 cm^{-1}, which can be attributed to the νCC stretch and βCH angular deformation, respectively. The amine group is characterized by νCN stretch at 1220 cm^{-1}. For pernigraniline the βCH band value is at 1157 cm^{-1}, and the authors suggest that this band can be used as a qualitative measure of the degree of oxidation of the PANI chain. Another characteristic band of pernigraniline

base is the stretch of C=N bond at 1480 cm^{-1}. Another way to determine the degree of oxidation of PANI, proposed by (Quillard et al., 1994; Berrada et al., 1995; Asturias et al., 1989), consists in determination of the intensities of the bands at about 1500 cm^{-1} for leucoesmeraldina (vCC) and the band around 1600 cm^{-1} for pernigranilina (vC=C) observed in the infrared spectra. The intensity ratio between these two bands (I(1600)/I(1500)) is a way to determine qualitatively the degree of oxidation in the chain of PANI.

(Louarn et al., 1996) performed a normal coordinate analysis of the emeraldine PANI salt, through the analysis of the infrared and Raman data of PANI with selective deuteration. The normal coordinate calculation confirms the assignments made by other authors and allowed to correlate the band at 1515 cm^{-1} to the angular deformation of NH group. The authors proposed the existence of bipolaronic segments (dications or protonated imines) to explain the Raman spectrum of emeraldine PANI salt obtained with laser line at 632.8 nm. The existence of these segments was also suggested by (Huang & MacDiarmid, 1993; McCall et al., 1990) through UV-VIS-NIR data and by other authors through spectroelectrochemical measurements monitored by *in situ* EPR (Geniés, 1987). The main issue posted by (Louarn et al., 1996) is that the doublet nature of the CN stretch (ca. 1320-1350 cm^{-1}) remains unclear. However, the authors suggest, like (Furukawa et al., 1988) that the origin of the doublet may be associated with the existence of two different conformations of PANI.

The Raman study of PANI doped with camphorsulfonic acid (CSA) and dissolved in *m*-cresol (Da Silva et al., 1999a; Da Silva et al., 1999b), named Secondary doping by (MacDiarmid & Epstein, 1995; MacDiarmid & Epstein, 1994; Xia et al., 1995), revealed a conversion of dications to radical cations. This behavior is justified by the increase of the polaronic band in ca. 1336 cm^{-1} and decrease of the intensities of the Raman bands at 1486 cm^{-1} and 1380 cm^{-1}, assigned to vC=N and vC=C modes of dications units, respectively using laser line at 632.8 nm. (M. Cochet et al., 2000) also investigated by resonance Raman spectroscopy, the secondary doping in PANI-CSA, trying to verify by normal modes calculations if the changes in the torsion angle between the benzene rings could explain the modifications in the Raman spectrum of PANI-CSA treated with *m*-cresol. But, the data could not be interpreted only in terms of flatness of the rings; the changes observed are also associated with changes in the electronic structure, leading to the appearance of new Raman bands and the modifications of others, due to, the high charge delocalization on the polymeric chains.

The major part of the Raman studies of PANI use laser lines in the visible region, (Sacricifti & Kusmany, 1987; Furukawa et al., 1988; Hugot-Le Goff & Bernard, 1993; Louarn et al., 1996; Colomban et al., 1999; Zhang et al., 2005; Trchová et al., 2006; Do Nascimento et al., 2002a; Do Nascimento et al., 2002b) but some Raman studies of PANI using near-infrared (NIR) laser line is also found (Engert *et al.*, 1994; Quillard *et al.*, 1995; Niaura et al., 2004). The most peculiar feature observed at 1064.0 nm is the presence of a sharp band around 1375 cm^{-1} in emeraldine base PANI spectrum, which was correlated by (Engert *et al.*, 1994) to polaronic segments localized at two benzene rings. On the other hand, (Quillard *et al.*, 1995) proposed that this band was not correlated with protonated segments but with over-oxidized segments such as those present in PANI as the pernigraniline base (PANI-PB). Some controversial aspects about the Raman spectra of poly(aniline) obtained at NIR radiation excitation were recently re-examined by (Do Nascimento & Temperini, 2008). The bands from 1324 to 1375 cm^{-1} were associated to vC–N of polarons with different conjugation lengths and with the presence of charged phenazine-like and/or oxazine-like rings in PANI-ES as chemically prepared. The formation of cross-linking structures is associated with the

ES form of PANI. The bands from 1450 to 1500 cm^{-1} in the PANI-EB and PANI-PB spectra were associated with the νC=N mode of the quinoid units having different conjugation lengths.

The thermal behavior of PANI has been also studied by vibrational spectroscopy. The Raman studies of PANI-CSA conducted by (Da Silva et al., 2000; Do Nascimento et al., 2002b) revealed that there is the appearance of intense bands at 574, 1393 and 1643 cm^{-1} in the Raman spectra at 632.8 nm during heating. These same bands were observed in the Raman spectra of a conducting polymer derived from PANI, the poly(diphenylamine) doped with HCSA (PDFA-CSA) during heating. It was observed that these bands are not present during the heating of polymers in vacuum. By comparing the results obtained from the thermal monitoring of PANI-CSA and PDFA-CSA, it was possible to assign these bands to the reaction of the polymer with oxygen, with formation of chromophores with oxazine-like rings. It was also demonstrated that the increase of laser power at 1064.0 nm causes deprotonation of PANI-ES and formation of cross-linking segments having phenazine and/or oxazine-like rings. The formation of cross-linking structures is associated with the ES form of PANI.

4. Results and discussion

4.1 PANI nanofibers obtained from micellar media

PANI has been largely prepared as nanofiber with the use of polymerization media containing organic acids that acts as surfactants (Zhang et al., 2002; Qiu et al., 2001; Wei & Wan, 2002; Do Nascimento et al., 2006; Zhang et al., 2009). A broad variety of organic acid has been employed in order to modulate the diameter of the resulting nanofibers. The FTIR spectra of PANI doped with various organic acids, containing sulfo-group (SO$_3$-H), show broad bands at about 3430 cm^{-1}, 1560 cm^{-1}, 1480 cm^{-1}, 1130 cm^{-1}, and 800 cm^{-1}, which are related to emeraldine PANI salt (Huang & Wan, 1999). The UV-vis spectra of all doped PANI samples show two polaronic absorptions around 400 and 800 nm. The position of polaronic bands shifts to a long wavelength when the size of organic dopant increases. For instance, the polaron absorption for the PANI doped with smaller dopant (α-NSA) is located at 800-900 nm. On the other hand, the polaron absorption for the doped PANI with larger dopant (β-NSA) is shifted to 1060-1118 nm.

The resonance Raman (RR) spectra (from 1000 to 1800 cm^{-1}) obtained for PANI nanofibers doped with NSA (β-naphtalenesulfonic acid), with different diameters, show similar spectral profile. This result indicates that the morphological differences in PANI-NSA nanofibers have small influence in the Raman spectra from 1000 to 1800 cm^{-1}. Comparing the RR spectra of PANI-NSA fibers to PANI-ES spectrum, bands at 1163 and 1330 cm^{-1} in PANI-NSA spectra can be associated with those at 1165 and 1317-1337 cm^{-1} in PANI-ES spectrum. These bands have been assigned to βC-H and νC-N of polaronic segments, respectively (Do Nascimento et al., 2006). Their relative intensities in PANI-NSA spectra increase as the molar ratio of β-NSA:aniline increases. Thus, the RR data of the PANI-NSA nanofibers show that the spectral changes observed among the as-prepared PANI-NSA samples are owing to differences in the protonation degrees. Similarly, (Wang et al., 2008) observed in that the bands at 1257 and 1337 cm^{-1}, assigned to C-N stretching modes of benzenoid and radical segments of doped PANI, respectively, increase their intensities with the increase of stearic acid used as soft template.

The Raman spectra of PANI nanofibers prepared in micellar media also show the presence of bands at ca. 578, 1400, and 1632 cm^{-1}. These bands were strictly correlated with the formation of cross-linking structures in PANI chains after heating in the presence of air (Do Nascimento et al., 2002b). Different studies show that the bands at ca. 578, 1400, and 1632 cm^{-1} are similar to those observed for dyes with phenoxazine ring. The presence of phenoxazine rings in PANI backbone was also observed by (Trchová et al., 2006 and Stejskal et al., 2006) in the study of formation of polyaniline nanotubes under different acidic media. The authors concluded that the presence of phenoxazine units is crucial for stacking and stabilization of the nanotube wall of PANI. Probably, the π-π stacking formed by phenoxazine rings, in the PANI backbone prepared in micellar media, is one of the driving forces for the formation of PANI chains with extended conformation and PANI particles with one-dimensional (needles and/or nanofibers) morphology. Thus, the presence of cross-linking structures in the PANI chains may be one of the characteristics of chains formed in micellar polymerization (Do Nascimento et al., 2008b).

On the comparison of the spectral behavior of PANI nanofibers/nanotubes prepared with NSA (β-naphtalenesulfonic acid) or with DBSA (dodecybenzenesulfonic acid) indicates that polymeric chains have a certain degree of extended conformation due to the presence of free-carrier absorption in the UV-VIS-NIR spectra. Hence, the presence of 609 cm^{-1} band in the PANI-NSA and PANI-DBSA Raman spectra indicates that these samples have a certain degree of extended conformation. The band at 609 cm^{-1} can be assigned to a vibrational mode related to benzene deformations or torsions. Probably, this mode is sensible to changes of the dihedral angle between neighbors benzene rings, or in other words, sensible to the conformation of the PANI chains (Do Nascimento et al., 2008b).

Electron microscopic images reveal the loss of the fibrous morphology of PANI after treatment of PANI-NSA samples with HCl solution in order to acquire higher doping state (Do Nascimento et al., 2006). However, further studies reveal that submitting the PANI-NSA to heating treatment at 200ºC, occurs the formation of a high degree of cross-linking structures, verified by the appearance of characteristic RR bands at 578, 1398 and 1644 cm^{-1}, hence the fibrous morphology is retained after the doping process (Do Nascimento et al., 2008c). The structure of PANI-CSA (CSA is the 1R-(−)10-camphorsulfonic acid) nanofibers was also investigated by solid state ^{13}C and ^{15}N nuclear magnetic resonance (NMR) (Hopkins et al., 2008). The results (compared to the unstructured, granular form of PANI) revealed a slight variation in the structural features of the polymer that led to some differences in the chemical environments of the respective nuclei. The presence of two extra-sharp peaks at 96.5 and 179.8 ppm is a distinct feature found exclusively in the nanofiber spectra and the presence of a complete set of sharp NMR peaks is a consequence of the more ordered morphology in the PANI nanofibers.

PANI nanofibers synthesized in ionic liquids have been studied by Raman spectroscopy. (Wei et al., 2006) obtained nanofibers of PANI by electropolymerization of aniline in BMIPF$_6$ (1-butyl-3-methyl-imidazolium hexafluorophosphate). The Raman spectra show that the PANI is similar to the emeraldine salt form. However, the intensity of the quinoid ring stretching at 1578 cm^{-1} is higher than that of the benzenoid band at 1469 cm^{-1}, indicating the existence of a higher amount of quinoid structures. The authors (Wei et al., 2006) suggest that the PANI film synthesized in this ionic liquid media is formed by small amount of non-conducting forms such as emeraldine base and/or pernigraniline forms, which have more quinoid structures in the backbone. The bands at 1578, 1386, and 1340 cm^{-1} were assigned to emeraldine PANI base; and the bands at 1606, 1469, 1252, and 1177 cm^{-1} to emeraldine salt form.

4.2 PANI nanofibers obtained from interfacial polymerization

More recently, uniform nanofibers of pure metallic PANI (30-120 nm diameters, depending on the dopant) have also been prepared by polymerization at an aqueous organic interface (Huang & Kaner, 2004a; Huang & Kaner, 2004b). However, it was often observed that the quality of the products such as the shape and stability of their dispersions varies with different synthetic conditions, such as, stirring, temperature and pH, among others. (Colomban *et al.*, 1999; Cochet *et al.*, 2000a; Cochet et al., 2000b) have been demonstrated that the low energy Raman bands from 100 to 600 cm^{-1} in the PANI spectra are very sensible to the crystalline arrangement and also to the conformational changes of the PANI chains. The Raman spectra of PANI nanofibers prepared from interfacial polymerization were obtained at low wavenumbers. It was observed that the bands at 200 and 296 cm^{-1}, related to C_{ring}-N-C_{ring} deformation and lattice modes of polaron segments of PANI with type-I crystalline arrangement (Colomban *et al.*, 1999), practically disappears in the Raman spectra of PANI nanofibers. This effect is very pronounced for the nanofiber sample prepared using 5.0 mol.L^{-1} HCl aqueous solution. The effects of HCl concentration over the bands at low wavenumbers (200 and 296 cm^{-1}) is strictly related to PANI samples prepared from interfacial polymerization. In addition, shifts of the bands from 393-427 cm^{-1} to 422-451 cm^{-1} are also seen for PANI nanofibers prepared with higher HCl concentration. (Cochet *et al.*, 2000a; Cochet et al., 2000b) demonstrated that mainly the bands at about 200-500 cm^{-1} are very sensible to the conformational changes. The shift to higher wavenumbers of the bands at about 400 cm^{-1} indicates the increase of the torsion angles of the C_{ring}-N-C_{ring} segments. Thus, the decrease in the intensities of the bands at 200 and 296 cm^{-1} and also the shift of the bands at about 400 cm^{-1} are due to the conformational changes in the PANI backbone. The FTIR spectra for PANI nanofibers display higher changes in the region from 2000 to 4000 cm^{-1} (Do Nascimento et al., 2008a). Mainly the bands related to NH_2^+ modes at 2480, 2830, and 2920 cm^{-1} increase in their intensities for PANI samples prepared with higher HCl concentration (higher than 1.0 mol.L^{-1}), consequence of the increase of protonated imine and amine nitrogens in the structure of PANI. The bands at about 3200 and 3450 cm^{-1} also change their relative intensities, being correlated to N-H stretching modes (the contribution of O-H stretching, due to the adsorbed water, is similar for all analyzed samples). The band at 3200 and 3450 cm^{-1} can be assigned to bonded N-H and free N-H stretching modes (Jana et al., 2003; Lunzy & Banka, 2000), showing that the contribution of the different types of hydrogen bonds are also changed by the increase of acidity of the synthetic media. The changes in the intensities associated with an increase in the torsion angles of C_{ring}-N-C_{ring} segments is owing to the formation of bipolarons (protonated, spinless units) in the PANI backbone higher than the PANI samples prepared by the conventional route (Geniés et al., 1990). The nanostructured surface of PANI permits major diffusion of the ions inside the polymeric matrix leading to a more effective protonation of the polymeric chain than the PANI prepared in the conventional way, leading to the reduction of crystallinity of PANI, and the decrease in the amount of nanofibers (Do Nascimento et al., 2008a).

5. Final remarks

The screening of the electronic and vibrational structure of the polyaniline nanofibers has been decisive in the studies related to the formation, interactions between the chains, properties and stabilities of the nanostructured polyaniline. Nowadays, two great approaches are used to acquire the PANI with nanostructured morphology without the use

of rigid hosts: (i) polymerization of aniline in a micellar media and (ii) polymerization of aniline on the interface between two solvents. However, the morphology of PANI obtained without rigid hosts is more susceptible to the synthetic conditions (such as pH) and also post-synthesis procedures. Mainly, it is observed shifts in the vibrational frequencies of polyaniline and also variations in their intensities. The presence of bands owed to phenoxazine rings is observed in PANI backbone formed in micellar media. The presence of phenoxazine units is crucial for stacking and stabilization of the nanotube wall of PANI. Probably, The π-π stacking formed by phenoxazine rings, in the PANI backbone prepared in micellar media, is one of the driving forces for the formation of PANI chains with extended conformation and PANI particles with one-dimensional (needles and/or nanofibers) morphology. Thus, the presence of cross-linking structures in the PANI chains may be one of the characteristics of chains formed in micellar polymerization. The changes in the intensities of the vibrational spectra at low energies are associated with an increase in the torsion angles of C_{ring}-N-C_{ring} segments due to the formation of bipolarons (protonated, spinless units) in the PANI backbone higher than the PANI samples prepared by the conventional route. The nanostructured surface of PANI permits major diffusion of the ions inside the polymeric matrix leading to a more effective protonation of the polymeric chain than the PANI prepared in the conventional way, leading to the reduction of crystallinity of PANI, and the decrease in the amount of nanofibers.

6. References

Asefa, T.; MacLachan, M. J.; Coombs, N. & Ozin, G. A. (1999). Periodic mesoporous organosilicas with organic groups inside the channel walls. *Nature*, 402, 867-871.

Bacon, J. & Adams, R. N. (1968). Anodic oxidation of aromatic amines. 3. Substituted anilines in aqueous media. *J. Am. Chem. Soc.*, 90, 24, 6596-6599, 0002-7863.

Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W. & Shirakawa, H. (1978). Synthesis of highly conducting films of derivatives of polyacetylene (CH)x. *J. Am. Chem. Soc.* 100, 3, 1013-1015, 0002-7863.

Chiang, C. K.; Fincher Jr, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J. & MacDiarmid, A. G. (1977). Electrical-conductivity in doped polyacetylene. *Phys. Rev. Lett.* 39, 17, 1098-1101, 31-9007.

Cochet, M.; Louarn, G.; Quillard, S.; Boyer, M. I.; Buisson, J. P. & Lefrant, S. (2000a). Theoretical and experimental vibrational study of polyaniline in base forms: non-planar analysis. Part I. *J. Raman Spectrosc.*, 31, 11, 1029–1039, 0377-0486.

Cochet, M.; Louarn, G.; Quillard, S.; Buisson, J. P. & Lefrant, S. (2000b). Theoretical and experimental vibrational study of emeraldine in salt form. Part II. *J. Raman Spectrosc.* 31, 11, 1041–1049, 0377-0486.

Colomban, Ph.; Folch, S. & Gruger, A. (1999). Vibrational study of short-range order and structure of polyaniline bases and salts. *Macromolecules*, 32, 9, 3080-3092, 0024-9297.

Davis Jr., J. H.; Gordon, C. M.; Hilgers, C. & Wasserscheld, P. (2002). Synthesis and Purification of Ionic Liquids, In: *Ionic Liquids in Synthesis*, Wasserscheid, P. & Welton, T. (Eds.), 7-40, Wiley–VCH, 3-527-60070-1, New York.

Do Nascimento, G. M.; Constantino, V. R. L. & Temperini, M. L. A. (2002a). Spectroscopic characterization of a new type of conducting polymer-clay nanocomposite. *Macromolecules* 37, 20, 7535-7537, 0024-9297.

Do Nascimento, G. M.; Da Silva J. E. P.; De Torresi, S. I. C. & Temperini, M. L. A. (2002b). Comparison of secondary doping and thermal treatment in poly(diphenylamine) and polyaniline monitored by resonance Raman spectroscopy. *Macromolecules*, 35, 1, 121-125, 0024-9297.

Do Nascimento, G. M.; Constantino, V. R. L.; Landers, R. & Temperini, M. L. A. (2004). Aniline polymerization into montmorillonite clay: A spectroscopic investigation of the intercalated conducting polymer. *Macromolecules*, 37, 25, 9373-9385, 0024-9297.

Do Nascimento, G. M.; Silva, C. H. B. & Temperini, M. L. A. (2006). Electronic structure and doping behavior of PANI-NSA nanofibers investigated by resonance Raman spectroscopy. *Macromol. Rapid Commun.*, 27, 4, 255-259, 1022-1336.

Do Nascimento, G. M.; Kobata, P. Y. G. & Temperini, M. L. A. (2008a). Structural and vibrational characterization of polyaniline nanofibers prepared from interfacial polymerization. *J. Phys. Chem. B*, 112, 37, 11551-11557, 1520-6106.

Do Nascimento, G. M.; Silva, C. H. B.; Izumi, C. M. S. & Temperini, M. L. A. (2008b). The role of cross-linking structures to the formation of one-dimensional nano-organized polyaniline and their Raman fingerprint. *Spectrochim. Acta A*, 71, 3, 869-875, 1386-1425.

Do Nascimento, G. M.; Silva, C. H. B. & Temperini, M. L. A. (2008c). Spectroscopic characterization of the structural changes of polyaniline nanofibers after heating. *Polym. Degrad. Stab.*, 93, 1, 291-297, 0141-3910.

Do Nascimento, G. M. & Temperini, M. L. A. (2008). Studies on the resonance Raman spectra of polyaniline obtained with near-IR excitation. *J. Raman Spectrosc.*, 39, 7, 772-778, 0377-0486.

Dupont, J. (2004). On the solid, liquid and solution structural organization of imidazolium ionic liquids. *J. Braz. Chem. Soc.*, 15, 3, 341-350, 0103-5053.

Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R. & Wildegren, J. A. (2006). The distillation and volatility of ionic liquids. *Nature*, 439, 7078, 831-834, 0028-0836.

Engert, C.; Umapathy, S.; Kiefer, W. & Hamaguchi, H. (1994). Dynamic structure of charge-carrier in polyaniline by near-infrared excited resonance Raman spectroscopy. Chem. Phys. Lett. 218, 1-2, 87-92, 0009-2614.

Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T. & Kawagoe, T. (1988). Vibrational-spectra and structure of polyaniline. *Macromolecules*, 21, 5, 1297-1305, 0024-9297.

Gao, H.; Jiang, T.; Han, B.; Wang, Y.; Du, J.; Liu, Z. & Zhang, J. (2004). Aqueous/ionic liquid interfacial polymerization for preparing polyaniline nanoparticles. *Polymer*, 45, 9, 3017-3019, 0032-3861.

Geniés, E. M.; Boyle, A.; Lapkowski, M. & Tsintavis, C. (1990). Polyaniline- A historical survey. *Synth. Met.*, 36, 2, 139-182, 0379-6779.

Han, C. C. & Elsenbaumer, R. L. (1989). Protonic acids- generally applicable dopants for conducting polymers. *Synth. Met.* 30, 1, 123-131, 0379-6779.

Heeger, A. J. (2001). Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials (Nobel Lecture) *Angew. Chem. Int. Ed.* 40, 14, 2591-2611, 1433-7851.

Hopkins, A. R.; Lipeles, R. A. & Hwang, S. J. (2008). Morphology characterization of polyaniline nano- and microstructures. *Synth. Met.* 158, 14, 594-601, 0379-6779.

Huang, J. & Kaner, R. B. (2004a). Nanofiber Formation in the chemical polymerization of aniline: a mechanistic study. *Angew. Chem. Int. Ed.*, 43, 43, 5817–5821, 1433-7851.

Huang, J. & Kaner, R. B. (2004b). A general chemical route to polyaniline nanofibers. *J. Am. Chem. Soc.*, 126, 3, 851–855, 0002-7863.

Huang, J. & Wan, M. (1999). Polyaniline doped with different sulfonic acids by in situ doping polymerization, *J. Polym. Sci.: Part A: Polym. Chem.*, 37, 1277–1284, 0887-624X.

Hugot-Le Goff, A. & Bernard, M. C. (1993). Protonation and oxidation processes in polyaniline thin-films studied by optical multichannel analysis and in-situ Raman-spectroscopy. *Synth. Met.*, 60, 2, 115-131, 0379-6779.

Jana, T.; Roy, S. & Nandi, A. K. (2003). High temperature d.c. conductivity of sulfonic acid doped thermoreversible polyaniline gels. *Synth. Met.* 132, 3, 257-264, 0379-6779.

Kusmany, H. & Sacriftci, N. S. (1987). In situ spectro-electrochemical studies of polyaniline. *Synth. Met.*, 18, 1-3, 353-358, 0379-6779.

Liepins, R. & Ku, C. C. (1987). *Electrical Properties of Polymers: chemical principles,* Hanser Publishers, 0029476313, New York.

Louarn, G.; Lapkowski, M.; Quillard, S.; Pron, A.; Buisson, J. P. & Lefrant, S. (1996). Vibrational properties of polyaniline - Isotope effects. *J. Phys. Chem.,* 100, 17, 6998-7006, 22-3654.

Lunzy, W. & Banka, E. (2000). Relations between the structure and electric conductivity of polyaniline protonated with camphorsulfonic acid. *Macromolecules* 33, 2, 425-429, 0024-9297.

MacDiarmid, A. G. (2001). "Synthetic Metals": a novel role for organic polymers (Nobel Lecture). *Angew. Chem. Int. Ed.* 40, 14, 2581-2590, 1433-7851.

MacDiarmid, A. G.; Chiang, J. C.; Richter A. F. & Sonosiri, N. L. D. (1987). *Conducting Polymers*, Alcácer, L. (Ed.), Reidel Publications, Dordrecht.

MacDiarmid, A. G. & Epstein, A. J. (1989a). Polyanilines- A novel class of conducting polymers. *Faraday Discuss. Chem. Soc.*, 88, 317-325, 1364-5498.

MacDiarmid, A. G. & Epstein, A. J. (1989b). The polyanilines: a novel class of conducting polymers In: *Conducting polymers, emerging technologies,* 27-35, Technical Insights, New Jersey.

MacDiarmid, A. G. & Epstein, A. J. (1994). Conducting polymers: Science and Technology, In: *Frontiers of Polymers and Advanced Materials,* Prasad, P. N. (Ed.), 251-261, Plenum Press, 978-0306447167, New York.

Mohilner, D. M.; Argersinger, W. J. & Adams, R. N. (1962). Investigation of kinetics and mechanism of anodic oxidation os aniline in aqueous sulfuric acid solution at a platinum electrode. *J. Am. Chem. Soc.*, 84, 19, 3618-3622, 0002-7863.

Niaura, G.; Mazeikiene, R. & Malinauskas, A. (2004). Structural changes in conducting form of polyaniline upon ring sulfonation as deduced by near infrared resonance Raman spectroscopy. Synth. Met. 145, 2-3, 105-112, 0379-6779.

Nigrey, P. J.; MacDiarmid, A. G. & Heeger, A. J. (1979). Electrochemistry of polyacetylene, (CH)X- Electrochemical doping of (CH)X films to the metallic state. *J. Chem. Soc.: Chem. Commun.* 14, 594-595, 0022-4936.

Peng, H.; Tang, J.; Pang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker, C. J.; Yang Z. & Lu, Y. (2005). Polydiacetylene/Silica nanocomposites with tunable mesostructure and

thermochromatism from diacetylenic assembling molecules. *J. Am. Chem. Soc.*, 127, 37, 12782-12783.

Qiu, H. J.; Wan, M. X.; Matthews, B. & Dai, L. M. (2001). Conducting polyaniline nanotubes by template-free polymerization. *Macromolecules*, 34, 4, 675-677, 0024-9297.

Quillard, S.; Berrada, K.; Louarn, G.; Lefrant, S.; Lapkowski, M. & Pron, A. In-situ Raman spectroscopic studies of the electrochemical behavior of polyaniline. (1995). *New J. Chem.*, 19, 4, 365-374, 1144-0546.

Rodrigues, F.; Do Nascimento, G. M. & Santos, P. S. (2007). Dissolution and doping of polyaniline emeraldine base in imidazolium ionic liquids investigated by spectroscopic techniques. *Macromol. Rapid Commun.*, 28, 5, 666-669, 1022-1336.

Sasaki, K.; Yaka, M.; Yano, J.; Kitani, A. & Kumai, A. (1986). Growth-mechanism in the electropolymerization of aniline and p-aminodiphenylamine. *J. Electroanal. Chem.*, 215, 1-2 401-407, 0022-0728.

Shirakawa, H. (2001). The discovery of polyacetylene film: the dawning of an era of conducting polymers (Nobel Lecture). *Angew. Chem. Int. Ed.* 40, 14, 2575-2580, 1433-7851.

Shirakawa, H. & Ikeda, S. (1971). Infrared spectra of poly(acetylene). *Polymer Journal* 2, 2, 231-244, 0032-3896.

Shirakawa, H. & Ikeda, S. (1974). Cyclotrimerization of acetylene by tris(acetylacetonato)titanium(III)-diethylaluminum chloride system. *J. Poylm. Sci. Chem.* 12, 5, 929-937, 0887-624X.

Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K. & Heeger, A. J. (1977). Synthesis of electrically conducting organic polymers-halogen derivatives of polyacetylene, (CH)X. *J. Chem. Soc.: Chem. Commun.* 16, 578-580, 0022-4936.

Song, J.; Cisar J. S. & Bertozzi, C. R. (2004). Functional self-assembling bolaamphiphilic polydiacetylenes as colorimetric sensor scaffolds. *J. Am. Chem. Soc.*, 126, 8459-8465.

Stejskal, J.; Sapurina, I.; Trchova, M.; Konyushenko, E. M. & Holler, P. (2006). The genesis of polyaniline nanotubes. *Polymer*, 47, 16, 8253-8262, 0032-3861.

Syed, A. A. & Dineson M. K. (1991). Polyaniline- A novel polymeric material- review. *Talanta,* 38, 8, 815-837, 0039-9140.

Trchová, M.; Matejka, P.; Brodinova, J.; Kalendova, A.; Prokes. J. & Stejskal, J. (2006). Structural and conductivity changes during the pyrolysis of polyaniline base. *Polym. Degrad. Stab.*, 91, 1, 114-121, 0141-3910.

Trchová, M.; Syedenkova, I.; Konyushenko, E. N.; Stejskal, J.; Holler, P. & Ciric-Marjanovic, G. (2006). Evolution of polyaniline nanotubes: The oxidation of aniline in water. *J. Phys. Chem. B*, 110, 19, 9461-9468, 1520-6106.

Wang, X.; Liu, J.; Huang, X.; Men, L.; Guo, M. & Sun, D. (2008). Controlled Synthesis of Linear Polyaniline Tubes and Dendritic Polyaniline Fibers with Stearic Acid. *Polym. Bull.* 60, 1, 1–6, 0170-0839.

Wasserscheid, P. & Keim, W. (2000). Ionic liquids - New "solutions" for transition metal catalysis. *Angew. Chem. Int. Ed.,* 39, 21, 3773-3789, 1433-7851.

Wawzonek, S. & McIntyre, T. W. (1967). Electrolytic oxidation of aromatic amines. *J. Electrochem. Soc.*, 114, 10, 1025-1029, 0013-4651.

Wei, D.; Kvarnstrom, C.; Lindfors, T. & Ivaska, A. (2006). Polyaniline nanotubules obtained in room-temperature ionic liquids. Electrochem. Commun. 8, 1563–1566,

Wei, Y.; Sun, Y. & Tang, X. (1989). Auto-acceleration and kinetics of electrochemical polymerization of aniline. *J. Phys. Chem.*, 93, 12, 4878-4881, 0022-3654.

Wei, Z. X. & Wan, M. X. (2002). Hollow microspheres of polyaniline synthesized with an aniline emulsion template. *Adv. Mater.*, 2002, 14, 18, 1314-1317, 0935-9648.

Zhang, H.; Wang, J.; Wang, Z.; Zhang, F. & Wang, S. (2009). A Novel Strategy for the Synthesis of Sheet-Like Polyaniline. *Macromol. Rapid Commun.*, 30, 1577-1582, 1022-1336.

Zhang, J.; Liu, C. & Shi, G. (2005). Raman spectroscopic study on the structural changes of polyaniline during heating and cooling processes. *J. Appl. Polym. Sci.*, 96, 3, 732-739, 0021-8995.

Zhang, Z. M.; Wei, Z. X. & Wan. M. X. (2002). Nanostructures of polyaniline doped with inorganic acids. *Macromolecules*, 35, 15, 5937-5942, 0024-9297.

Nanofibers

Edited by Ashok Kumar

"There's Plenty of Room at the Bottom" this was the title of the lecture Prof. Richard Feynman delivered at California Institute of Technology on December 29, 1959 at the American Physical Society meeting. He considered the possibility to manipulate matter on an atomic scale. Indeed, the design and controllable synthesis of nanomaterials have attracted much attention because of their distinctive geometries and novel physical and chemical properties. For the last two decades nano-scaled materials in the form of nanofibers, nanoparticles, nanotubes, nanoclays, nanorods, nanodisks, nanoribbons, nanowhiskers etc. have been investigated with increased interest due to their enormous advantages, such as large surface area and active surface sites. Among all nanostructures, nanofibers have attracted tremendous interest in nanotechnology and biomedical engineering owing to the ease of controllable production processes, low pore size and superior mechanical properties for a range of applications in diverse areas such as catalysis, sensors, medicine, pharmacy, drug delivery, tissue engineering, filtration, textile, adhesive, aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, information technology, photonic structures and flat panel displays, just to mention a few. Nanofibers are continuous filaments of generally less than about 1000 nm diameters. Nanofibers of a variety of cellulose and non-cellulose based materials can be produced by a variety of techniques such as phase separation, self assembly, drawing, melt fibrillation, template synthesis, electro-spinning, and solution spinning. They reduce the handling problems mostly associated with the nanoparticles. Nanoparticles can agglomerate and form clusters, whereas nanofibers form a mesh that stays intact even after regeneration. The present book is a result of contributions of experts from international scientific community working in different areas and types of nanofibers. The book thoroughly covers latest topics on different varieties of nanofibers. It provides an up-to-date insightful coverage to the synthesis, characterization, functional properties and potential device applications of nanofibers in specialized areas. We hope that this book will prove to be timely and thought provoking and will serve as a valuable reference for researchers working in different areas of nanofibers. Special thanks goes to the authors for their valuable contributions.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

INTECH
open science | open minds