### Chapter 1. INTRODUCTION

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1.1. Introduction

An organic polymer that possesses the electrical properties of a metal while retaining its mechanical properties and processability, is termed an ‘intrinsically conducting polymer’ (ICP). The common feature of most ICPs is the presence of alternating single and double bonds along the polymer chain, which enable the delocalization or mobility of charge carriers along the polymer backbone. These polymers are rendered conductive by the doping process involving the reaction of conjugated polymer with an oxidizing agent, a reducing agent or a protonic acid, resulting in highly delocalized polycations or polyanions. The real breakthrough in the development of conjugated organic conducting polymers was made by the discovery of metallic conductivity in polyacetylene films with halogen dopants in a collaborative research work performed by Hideki Shirakawa, Alan G. MacDiarmid and Alan J. Heeger in 1977 [1]. The importance and potential impact of this new class of material was soon recognized by the world scientific community and the Nobel Prize in Chemistry for the millennium year 2000 was awarded for their research on conducting polymers [2-5]. The conductivity of ICPs lies above that of insulators and extends well into the region of common metals; therefore, they are often referred to as ‘synthetic metals’.

1.2. Doping-induced conductivity of organic polymer

In order to make polymers electronically conductive, it is necessary to introduce mobile charge carriers into the conjugated system through a process known as doping.

Doping of a conducting polymer involves the introduction of a large amount of electron donor or acceptor. Doping involves either oxidation or reduction of the polymer backbone. Oxidation removes electrons and produces a positively charged polymer (p-doped) while reduction adds electrons and produces a negatively charged backbone (n-doped). The oxidation and reduction reactions can be induced either chemically or
electrically. The presence of large amount of dopant and the consequent structural changes in the polymer result in a material that is significantly different from the non-doped or undoped material. The dopant perturbs the polymer backbone extensively not only because of its significant physical size but also the extensive charge transfer that takes place between the polymer chain and the dopant, leading to changes in the geometry of the chain.

1.3. Representative candidates of conducting polymers

There are several families of polymers of different chemical nature like polene-type, aromatic, heteroatomic and mixed aromatic (or heteroaromatic) systems and others [6]. Representative candidates of conducting polymers are displayed in Fig. 1.1. The DC conductivity of a number of ICPs relative to copper and liquid mercury is presented in Fig. 1.2 and their DC conductivity, stability and processability are summarized in Table 1.1 [7,8].

![Chemical structures of conducting polymers]

**Figure 1.1.** The chemical structures of several kinds of ICPs.

![DC conductivity of ICPs]

**Figure 1.2.** The DC conductivity of a number of ICPs relative to copper and mercury.
Table 1.1. The DC conductivity, stability and processability of doped ICPs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>DC conductivity (Scm(^{-1}))</th>
<th>Stability</th>
<th>Processability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td>(10^3-10^5)</td>
<td>Poor</td>
<td>Limited</td>
</tr>
<tr>
<td>Polyphenylene</td>
<td>1000</td>
<td>Poor</td>
<td>Limited</td>
</tr>
<tr>
<td>Poly(phenylene vinylene)</td>
<td>1000</td>
<td>Poor</td>
<td>Limited</td>
</tr>
<tr>
<td>Poly(phenylene sulphide)</td>
<td>100</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
<tr>
<td>Polypyrroles</td>
<td>100</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Polythiophenes</td>
<td>100</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Polyaniline</td>
<td>10</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

1.4. Applications of conjugated conducting polymers

Conducting polymers are attractive materials for use in existing and emerging technologies due to their light weight, low cost and versatility compared to other standard conductors and semiconductors [7,8]. Some examples of potential applications include rechargeable batteries, electrochromic displays, light emitting diodes, sensors, field effect transistors, electromagnetic interference shielding, anticorrosion materials, microwave absorption, static electricity dissipation, etc. [7]. Several applications have been proposed in power equipment areas such as solid dielectric cable, oil-filled cable, capacitors, transformers, rotating machines, bushings, surge suppressors, vacuum interrupters, gas insulating equipment and other applications. The most promising applications of conducting polymer blends are in capacitors, rotating machines, bushings, and gas-insulated equipment. In particular, the following applications score high in the ranking system: coating of dielectric films for capacitors, coating of a conducting compound to cover conductors in rotating machines, surface coatings to dissipate charge in bushings, coatings for controlled surface conductivity in gas-insulated equipment and thermal history monitors [8].
1.5. Polyaniline

1.5.1. Origin and development

Earlier the monomer aniline was obtained from the pyrolytic distillation of indigo and was called ‘Krystallin’ because it produced well-formed crystalline salts with sulfuric and phosphoric acids. In 1840, Fritzsche also obtained colorless oil from indigo, called it aniline ostensibly from the Spanish añil (indigo) and oxidized it to polyaniline (PANI). Some believe this to be the first report of PANI, although the first definitive report did not occur until 1862 when Letheby published his work [9]. During the early 20th century, occasional reports about the structure of PANI appeared in the literature and continued periodically until 1980s. It was during this time that MacDiarmid reinvestigated the previous work of Josefowicz and ‘discovered’ in 1985 that PANI can be made electrically conducting upon protonic doping [10]. In subsequent years, the study of PANI exploded and currently a vast literature on synthesis, properties and applications of PANI exists. Although it was discovered some 150 years ago by Letheby [9], PANI has attracted renewed interest in fundamental science and industry over the past decade. Scientific interest in PANI originates from the fact that this conjugated polymer is unique in its class due to its ease of synthesis, relative environmental stability towards air and moisture, high conductivity, unique electronic, thermoelectric and optical properties, low cost and tunable electrical properties.

1.5.2. Synthesis

Conducting PANI materials are generally synthesized via the chemical oxidation of monomer route while the electrochemical and interfacial methods are also employed next to chemical method.
Chemical synthesis

Chemical polymerization is typically carried out with relatively strong chemical oxidants like ammonium persulfate, ferric ions, permanganate or dichromate anions, or hydrogen peroxide in acidic medium [11]. These oxidants are able to oxidize the monomer in solution, leading to the formation of cation radicals. These cation radicals further react and combine with other monomers or n-mers in head-to-tail mechanism, yielding oligomers or insoluble polymer. The counterion of the oxidants ultimately ends up as a dopant or co-dopant in the polymer. The powerful oxidant also makes it difficult to control the oxidizing power in the reaction mixture and in turn the degree of oxidation during synthesis. However, chemical synthesis has the advantage of producing bulk quantities of polymer materials on batch basis. To date it has been the major commercial method for producing such materials. Both the type of dopant and the level of doping are known to impact upon final properties of the polymer. Polymerization steps are shown in Chart 1.1 and the reaction mechanism of polymer growth is given in Scheme 1.1 [12].

![Chart 1.1. Polyaniline preparation by chemical method.](image)
Emulsion polymerization

In the emulsion polymerization first the emulsion of monomer is formed by dispersing it in organic-aqueous phase and stabilized with a surfactant and then the polymerization reaction is carried out with the initiator [7]. For example, in the synthesis of PANI by emulsion polymerization, an emulsion of aniline along with a protonic acid, an oxidant, an emulsifier (detergent), initiator and a nonpolar or weakly polar solvent, for example, xylene, chloroform, or toluene (sparingly soluble or insoluble in water) is formed. In some instances to form an emulsion, a protonic acid such as dodecylbenzene sulfonic acid is employed, which has a substantial emulsifying ability in weakly polar solvents. PANI salt exists in the emulsion along with other by-products. In most cases,
the product is isolated by destabilizing the emulsion through the addition of acetone. The PANI salt is then collected and subjected to repeated washing to free it from other constituents.

The advantage of this method over other polymerization processes is that the molecular weight of the polymer can easily be controlled by the addition of chain transfer agents; thus there can be control over the properties of the final product. Ruckenstein and Yang [13] have reported an emulsion pathway for the preparation of PANI–polystyrene composites.

The inverse emulsion polymerization process involves the formation of an aqueous solution of the monomer aniline, which is emulsified in a nonpolar organic solvent, for example, chloroform, toluene or in a mixture of solvents. The polymerization is then initiated with an oil-soluble initiator such as APS, benzoyl peroxide and so on. During the polymerization both a high molecular weight and high reaction rate can be simultaneously achieved. The solution is then treated with anhydrous sodium sulfate to remove the excess water. The viscous organic solution is then added to acetone or other suitable solvent in order to break the emulsion and precipitate PANI [7].

*Dispersion polymerization*

Dispersion polymerization may be defined as the polymerization of a monomer dissolved in an organic liquid or water to produce an insoluble polymer in the form of a stable colloidal dispersion. The colloidal stability of the resulting particle is provided by the adsorption of an amphilic polymeric stabilizer or a dispersant, which is present in the organic medium on the surface of the polymeric particles. Gill *et al* [14] have used a dispersion polymerization method to prepare stable PANI–silica colloidal composites. This method employs the controlled aggregation of colloidal silica to form the composite particles.


**Electrochemical synthesis**

The electrochemical synthesis of conducting polymers, first demonstrated with polypyrrole [15], has proven importance in the development of the field. Using this approach, semiconducting polymers have been obtained from a wide variety of monomers. A wide range of anodes may be employed, including platinum, gold, carbon, stainless steel and indium-doped tin oxide (ITO)-coated glass and the electrochemical synthesis is generally accomplished by potentiostatic or galvanostatic method. The advantage of the electrochemical route is that the PANI material is obtained in the form of a freestanding film; such films are often needed for technological applications. In the electrochemical synthesis, the monomer, the solvent and the electrolyte anion diffuse to the anode, polymerization starts in the interface between the electrode surface and the bulk. Electrochemical synthesis is cleaner and the polymer composite film can easily be peeled off from the electrode and washed.

**Photochemical and Bio-catalyzed synthesis**

Alternative routes to synthesize ICPs are photochemical and bio-catalysis methods. In photochemical method, the monomer and the solvent mixture is irradiated with visible light using either [Ru(bipy)$_3$]$^{2+}$ (bipy=2,2′-bipyridine) or [Cu(dpp)$_2$]$^+$ (dpp=2,9-diphenyl-1,10-phenanthroline) as the photosensitizer and an appropriate electron acceptor (sacrificial oxidant). Also PANI has been synthesized by using a laser and a gold electrode in a solution containing aniline under an applied external bias [16]. The morphology of the conducting polymer is strongly dependent on the excitation wavelength.

The enzyme horseradish peroxidase has been used for the polymerization of aniline in the presence of hydrogen peroxide through oxidative free radical coupling reactions [17]. Soybean peroxidase is an oxidoreductase enzyme capable of oxidizing
aromatic amines in the presence of hydrogen peroxide [18]. The advantage of this synthetic approach is that the polymerization of aniline can be carried out in environmentally mild conditions compared with chemical and electrochemical methods.

**Interfacial polymerization**

Interfacial polymerization (IP) involves step polymerization of a reactive monomer with an oxidizing agent, which are dissolved in two immiscible phases (organic and aqueous) and the reaction takes place at the interface of two liquids [19]. IP is commonly performed with volatile organic solvent as the organic phase, e.g., dichloromethane, chloroform, benzene, toluene, etc. The major advantages of IP compared with conventional polymerization in aqueous solution are the slow reaction rate resulting in nanostructures with a narrow size distribution and the ability to add various surfactants either organophilic or hydrophilic in organic or in aqueous solvent.

**Seeding polymerization**

The seeding polymerization is a typical template approach where a foreign material is used as the seed. By adding a small amount of any seed like PANI nanofibers (~50 nm), the single-walled carbon nanotubes (~20 nm), nanofibrous hexapeptide (12 nm) and the V$_2$O$_5$ nanofibers (~15 nm), into the reacting solution of aniline and APS, Zhang et al [20] performed the so-called ‘nanofiber seeding’ method for preparation of PANI nanofibers. The morphology of these nanofibers depends upon the type of acid used, acid concentration, type of seed, solvent used and the relative amount of seed with respect to solvent.

**Sonochemical synthesis**

The sonochemical process is accomplished with the aid of ultrasonic irradiation in the conventional method. Jing et al synthesized polyaniline nanofibers with high polymer yields using this technique [21].
**Plasma polymerization**

In plasma polymerization aniline monomer or a dispersion of monomer-droplets is first injected directly in the stream of plasma induced by a DC-glow discharge reactor. In the second step, the reactor is specially reconfigured to have a deposition of polymer particles in mild conditions. It is a solvent-free process and a pinhole-free coating can be obtained [22].

**Radiolytic synthesis**

In this method, the aqueous solution of aniline and APS in HCl is irradiated with gamma rays without any template [23]. PANI nanofibers decorated with metal nanoparticles are also prepared with the same gamma irradiation procedure. Thin films of PANI nanofibers are synthesized by ultraviolet irradiation of a spin-coated mixture of aniline nitric acid and APS on the surface of a silicon wafer.

**1.5.3. Soft and hard-templated method of synthesis**

The fabrication of nanostructures has been of increasing interest for its applications in many fields, including magnetics, electronics, biology, catalysis and optics. Nano/microstructured conducting polymers can be prepared by template-synthesis method [24]. Generally, the template synthesis, which involves hard template or soft template, is considered to be the most effective route to prepare nanostructured conducting polymers. The diameter of nanostructures is determined by the size of the pores in hard template. Although inorganic aluminum oxide, zeolite with channels and polymer membranes with porosity are commonly used as hard-templates, their preparation and the post-processing procedure for removing template are rather tedious, especially the oriented structures would be disturbed during the post-processes [25].

As in most examples where silica or alumina templates are used, the removal of these templates can be easily achieved by using hydrofluoric acid and strong bases or
acids, respectively. The most straightforward process would just involve a simple mixing of organic compound with inorganic template. In most cases host/guest polymerization reactions are used. Here the template is mixed together with a monomer melt or solution, yielding either a suspension of the template in the monomers (endotemplates e.g., silica, colloidal particles, cyclodextrin, etc.) or the incorporation of the monomers in the pores of the template (exotemplates e.g., zeolite, alumina, mesoporous silica, etc.) [26]. Scheme 1.2 shows the templating synthesis with a pictorial illustration [27].

The soft-template method is advantageous because an external template and post-treatment can be omitted [28]. Low-dimensional nanostructures of PANI in various shapes and forms such as nanoparticles, nanotubes, nanofibers and even spheres have been successfully synthesized by soft-template method [29]. ‘Templating’ essentially involves the replication of one structure into another under structural inversion. In the context of material chemistry, a template is a structure-directing agent. Templating, therefore, is a versatile technique for the formation of nanostructured or porous materials, as size and shape of the resulting pore structures can be easily tuned by choosing the appropriate template structures.
Li et al have reported a novel approach to prepare self-assembly of micro/nanowires of PANI-DNA hybrid with conductivity as high as $1.3 \times 10^{-2}$ S cm$^{-1}$ using DNA as dopant and a hard or soft-template [30]. Zhang and Liu have fabricated hollow PANI nanoparticles via the chemical oxidative polymerization of aniline by using $\gamma$-Fe$_2$O$_3$ nanoparticles as the reactive templates in the presence of hydrochloric acid [31].

1.5.4. Blends and composites

PANI is a promising material for several applications. However, its mechanical properties do not meet the requirements of a number of applications because, like other conducting polymers, it is not readily processable. Therefore, researchers have attempted to form PANI blends and composites with improved processability and mechanical properties while maintaining the inherent electroactive properties of the polymer.

Conducting PANI blends and composites are prepared mostly through the chemical oxidation of aniline in the presence of a host polymer or copolymer. Mixtures of materials can be homogeneous or heterogeneous. In the case of polymers, the homogeneous mixtures are classified by plastic technologists as blends and the heterogeneous as composites. Preparation methods include mechanical mixing, casting of a solution containing the components of the blend or polymerization of one polymer into the other. The last method can be achieved either chemically or electrochemically, producing blends or interpenetrating polymer networks and composites.

Broadly, the PANI blends and composites can be classified as follows:

1. Blends/composites with other polymers like PVP, PVA, PVC, polystyrene, etc.
2. Blends/composites with lengthy polymers like organic molecules, surfactants such as, SDBS, SDS, DNA, etc.
3. Composites with inorganic metal salts/complexes/compounds.
4. PANI intercalated composites with silica, zeolite and clay-like materials.
**Blends**

Synthesis of blends has become very important to obtain new class of materials recently. A great number of blends of conducting polymers have been successfully investigated in recent years. Several recent review articles deal with the chemical and electrochemical preparations of PANI blends as well as their properties and applications. Blends of PANI with neutral polymers such as PVP, PMAA, PVC, PVA, etc. constitute a very useful approach for the development of conducting materials with good mechanical properties. The soft-templates such as SDBS, SDS, DNA, CSA, NSA, cellulose derivatives, sucrose derivatives, polyurethane, polystyrene, ethylene vinyl acetate copolymer, polycarbonate, methane sulfonic acid, methyl orange, etc. are also used to synthesize PANI blends with high solubility and conductivity [32].

**Composites**

Composites are generally defined as the mixture of two immiscible materials. Zheng et al have developed a simple and repeatable PANI –TiO$_2$ composite-based gas sensor [33]. Joubert et al have synthesized various conducting composites, e.g., poly(butyl acrylate)- PANI doped with HCl, H$_2$SO$_4$ and H$_3$PO$_4$ which were tested in sensor devices and studied for their temperature-dependent conductivity [34]. Zhou et al have fabricated composites with core-shell structures consisting of PANI and multi-wall carbon nanotubes (MWCNT) and studied supercapacitor properties [35]. A critical account of the various blends and composites of PANI material has been presented in ref. 36.

**1.5.5. Structure**

PANI is a phenylene-based polymer having –NH– group on either side of the phenylene ring. Oxidation and reduction takes place on this –NH– group and various forms are obtained. The product formed is a simple 1,4-coupling of the monomer.
The molecular structure and different redox forms of PANI are illustrated in Fig. 1.3. It consists of ‘y’ reduced (benzenoid diamine) and ‘1-y’ oxidised (quinoid diamine) repeating units [37].

**Figure 1.3.** (a) Molecular structure and (b)–(e) Different redox forms of PANI.

Table 1.2 lists different redox forms of PANI [37]. Leucoemeraldine (LE) is a fully reduced state and is very reactive with the environment. It reacts even with a minute amount of oxygen and is environmentally unstable. Pernigraniline (PG) is a fully oxidized state with imine links instead of amine links and hence further oxidation is not possible. But pernigraniline base unlike LE is environmentally stable. The emeraldine form of PANI, often referred to as emeraldine base (EB), is either neutral or doped, with imine
nitrogens protonated by an acid. Emeraldine base (partially oxidized) is environmentally stable and does not undergo any change in chemical structure on prolonged storage. EB is regarded as the most useful form of PANI due to its high stability at room temperature and moreover its doped form (emeraldine salt; ES) is electrically conducting. LE and PG are poor conductors, even when doped with an acid. These forms may be inter-converted by chemical or electrochemical oxidation or reduction process.

<table>
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<tr>
<th>Form of PANI</th>
<th>Redox state</th>
<th>Color</th>
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<tbody>
<tr>
<td>Leucoemeraldine</td>
<td>Completely reduced</td>
<td>Yellow</td>
</tr>
<tr>
<td>Emeraldine</td>
<td>Partially oxidized</td>
<td>Green/Blue</td>
</tr>
<tr>
<td>Pernigraniline</td>
<td>Completely oxidized</td>
<td>Violet</td>
</tr>
</tbody>
</table>

1.5.6. Dopant effect on the structure of polyaniline

Doping is accomplished by the chemical method of direct exposure of the conjugated polymer to a charge transfer agent (dopant) in the solution/gas phase or by direct electrochemical oxidation or reduction or by interfacial method. The doping process is generally quantitative and charge carrier concentration is directly proportional to the dopant concentration. Dopants not only maintain charge neutrality but also bring about a geometry relaxation in the polymer chain and generate charge carriers. The properties of conducting PANI depend strongly on the doping level, i.e., the protonation level and size of the dopant. The dopants, according to their chemical nature, may be classified as ionic doping, organic dopants, neutral dopants and polymeric dopants.
Primary and secondary dopants

Primary dopant for PANI is a substance directly interacting with protonated imine centre and a relatively small quantity of it drastically changes the electronic, optical, magnetic and structural properties of the polymer. Polymer doping is always accompanied by a large increase in conductivity. Examples of primary dopants are mineral acids, organic acids, salts and polymeric ions. Secondary dopant is an apparently ‘inert’ substance which indicates still further changes in the properties of polymers when added to a primary-doped polymer [38]. Examples are DBSA, camphorsulfonic acid (CSA), polystyrene sulfonate, neutral polymers such as PVA, PAA, PVP, etc. A secondary dopant differs from a primary dopant in that the newly enhanced properties may persist even upon complete removal of the secondary dopant.

1.5.7. Formation of charge carriers and conduction process in polyaniline

To explain the electronic phenomenon of doping, new concepts including polarons and bipolarons were proposed by solid-state physicists. The presence of these species in PANI structures is shown in Fig. 1.4, where A⁻ represents the dopant ion. In PANI, a polaron structure is formed after protonation of the emeraldine base with different acids and is converted into emeraldine salt in which a polaron is formed through the successive formation of bipositive species (Fig. 1.4a), polaron structure (Fig. 1.4b) and more stable polaron structure (Fig. 1.4c) [39].

The conductivity of PANI in emeraldine salt form could be explained as follows: In the polaron structure, a radical cation of nitrogen acts as a hole and it is a charge carrier. The electron from the adjacent nitrogen (neutral) jumps into a hole and the hole then becomes neutral. Consequently, the holes now start to move as shown schematically in Fig. 1.5, leading to an electrical conduction along the chain. However, in the case of a
bipolaron structure, this type of movement of the electron and hole is not possible since the two holes are adjacently located [8].

\[ \sigma = en\mu \quad \text{(1.1)} \]

\( 'e' \) is the electronic charge \( (1.6 \times 10^{-19} \text{ C}) \), \( 'n' \) in \( \text{m}^{-3} \) and \( '\mu' \) in \( \text{m}^2/(\text{V-s}) \) [40]. The experimental results show that the majority charge carriers in PANI are holes, which indicates that the polyaniline is a \( p \)-type semiconductor [41]. The delocalized \( \pi \) bonds available in the system are responsible for the semi-conducting properties.

**Figure 1.4.** Structures of PANI, (a) emeraldine salt-bipolaron (poor charge mobility) state, (b) polaron (localized) state and (c) polaron (delocalized) state.

**Figure 1.5.** Representation of conduction pathway of PANI (the +ve sign represents the radical cation acting as a hole and the –ve sign represents neutral nitrogen).
The $\pi$ orbital produces the valence band and the $\pi^*$ forms the conduction band. The difference in energy between ground ($\pi$) and excited ($\pi^*$) orbitals is called the band gap or band energy. The value of this band gap determines both the electrical and optical properties of semi-conducting polymers. As the band gap energy decreases, the $\pi-\pi^*$ transition becomes easier, resulting in a high conductivity. The band gap energy of PANI could be estimated from UV-visible spectral analysis [42].

**Factors influencing the electrical conductivity**

The four factors in the order of their importance in determining conductivity are: (i) oxidation level and molecular arrangement, (ii) percentage of doping and type of dopant, (iii) percentage of crystallinity and inter-chain separation and (iv) molecular weight [42].

**AC conductivity**

The DC and AC charge transports occur both by the same mechanism. By hopping backward and forward at places with high jump probability, a charge carrier may significantly contribute to the AC conductivity. Complex impedance spectroscopy (CIS) is a very useful technique for the investigation of such process, because it can resolve the conduction components by differentiating between the transport properties of complex systems [43]. PANI, both in its base and salt forms, has been studied for its AC electrical and dielectric properties [44].

**1.6.2. Spectral studies**

**Fourier transform infrared (FTIR) spectra**

FTIR spectroscopy can provide a variety of information on structure, purity, redox and doping levels, hydrogen bonding, etc. The conversion of PANI emeraldine salt to base or vice versa can be followed by FTIR studies. The characteristic vibrational peaks of PANI have been reported in many studies and a recent one is ref. 45.
They are as follows: The peaks at 1559 and 1471 cm$^{-1}$ are assigned to C=C stretching vibrations of quinoid and benzenoid rings respectively. Imine and secondary amine peaks are observed at 1300 and 1230 cm$^{-1}$ respectively. The peak at 1121 cm$^{-1}$ corresponds to in-plane bending vibration of C–H which occurs during protonation. The peak at 798 cm$^{-1}$ originates from out-of-plane C–H bending vibration of 1,4-disubstituted benzene ring. The peaks at 800–900 cm$^{-1}$ are characteristic of para-substitution of the aromatic ring, which indicate that the polymerization proceeds via head-to-tail mechanism.

**UV-visible spectra**

Generally, conducting polymers have a broad UV-visible adsorption band, due to the conjugated chain structure. The various types of transitions of polyaniline are usually exhibited as peaks at 300-350 nm (sharp), 400-450 nm (shoulder), 600-650 nm (broad band) and 800-900 nm (broad band/shoulder). They are assigned to $\pi-\pi^*$ transitions indicating charge delocalization, polaronic transition associated with semiquinone radical, exciton or $n-\pi^*$ (polaron band) transition of emeraldine base and high wavelength polaron band or $\pi$-polaron transition of emeraldine salt respectively [46]. After combining with other components to form blends/composites, the $\pi$–polaron transition is usually shifted to a lower wavelength, revealing interactions between components and the quinoid rings of PANI [47].

**Nuclear magnetic resonance (NMR) spectra**

NMR is an equally powerful tool like FTIR. NMR study of PANI samples with different probes ($^1$H, $^{13}$C and $^{15}$N) yield useful information on the different oxidation states of PANI and structural and chemical changes taking place during doping and dedoping processes. Kaplan et al [48] have reported $^{15}$N NMR spectra of PANI which elucidated the structures of leucoemeraldine and emeraldine base. They observed a single resonance peak at 54.2 ppm confirming the existence of single –NH group in
leucoemeraldine and two peaks at 61 ppm and 62.3 ppm respectively for an emeraldine base and a salt.

**Mössbauer spectra**

The magnetic properties of doped PANI with FeCl₄/SnCl₄ were investigated by Mössbauer spectroscopy [49]. This study reports two findings: (i) an antiferromagnetic interaction occurs between the d-electrons of Fe³⁺ and π-electrons of PANI chain and (ii) PANI becomes soluble in nitromethane via complexation with SnCl₄.

**Electron spin resonance (ESR) spectra**

The doping process causes chemical modification of PANI resulting in the creation of charge carriers and unpaired π electrons inducing paramagnetism and transition from semiconducting to metallic state. The ESR spectroscopy clarifies these aspects by (i) intensity of ESR signal, (ii) g-tensor and (iii) line width. The intensity of ESR absorption corresponds to spin concentration. The g-tensor depends upon the paramagnetic species present and its value is a function of the spin environment. The g-tensor value for conducting PANI has been determined and is around 2.0, which is consistent with the presence of semiquinone radicals in PANI materials. The line width from peak to peak (ΔHpp) depends on the charge relaxation time [50].

**Raman spectroscopy**

Different redox forms of PANI, prepared either by chemical synthesis or by electrochemical procedures, have been studied with Raman spectroscopy and appropriate assignments of Raman bands have been made [51]. Various effects and phenomena characteristic of PANI have also been studied by *in situ* or *ex situ* Raman spectroscopy and spectroelectrochemistry, including the polaron state, protonation and oxidation processes.
Circular dichroism spectra

Dextro (D) or Leavo (L) camphorsulfonic acid (CSA) is the most used chiral dopant for the formation of chiral PANI, polypyrrole (Ppy) and their nanocomposites, because it could induce the helical conformation of PANI and Ppy by either post processing or in situ polymerization methods. Li et al have prepared chiral PANI/PAA/CSA nanocomposites using Poly(acrylic acid) (PAA) as a template and CSA as chiral inducing agent [52]. Yan et al clearly observed helical PANI nanofibers induced by large amounts of CSA dopant [53]. SEM images showed that the dopant D-CSA induced right-handed helical PANI nanofibers, while L-CSA produced left-handed helical PANI nanofibers. The corresponding circular dichroism spectra of the two kinds of PANI nanofibers were mirror images.

1.6.3. X-ray diffraction

X-ray diffraction (XRD) is the principal method used to identify the phases present in a solid state material. PANI is a semi-crystalline, heterogeneous system with a crystalline (ordered) region/domain dispersed in an amorphous (disordered) region as shown in Fig. 1.6 [8].

For PANI samples, the XRD peaks were reported at about $2\theta = 10^\circ$, $15^\circ$, $20^\circ$, $25^\circ$, $26^\circ$ and $30^\circ$, corresponding to (001), (011), (020), (200), (121) and (022) reflections in its emeraldine salt form, respectively [32]. The two broad peaks centered at $20^\circ$ and $25^\circ$, correspond to the periodicity parallel and perpendicular to the polymer chain, respectively. Scherrer formula is used to measure the crystallite size. Crystallite sizes upto 200 nm can be measured using Scherrer formula. In 5-50 nm, the broadening is easy to determine. For smaller particle sizes, low angle peaks are used for size determination as they are less broad as compared to large angle peaks [54].
1.6.4. Nanostructures

Different nanostructures have been reported for PANI and its blends/composites. A brief account is given below.

Granules

The granular morphology is the most common in PANI prepared by precipitation polymerization when using strong oxidants and high aniline concentrations under strongly acidic conditions [32], at pH < 2.5. Sometimes granular objects are referred to as nanospheres but they are not true nanospheres as observed in other experiments. PANI nanospheres having a diameter below 200 nm have occasionally been observed to accompany PANI nanotubes [32].

Nanofibers

Nanofibers are one-dimensional objects with a typical diameter of tens of nanometres. The term ‘nanowires’ is occasionally used as synonym for nanofibers. Their diameter is typically 20-100 nm, the length extends to several micrometres. Nanofibers are often branched and produce networks, arrays, bundles and more complex hierarchical structures [32].

Figure 1.6. Crystalline (ordered) and amorphous (disordered/poor crystalline) domains in a heterogeneous structure of PANI [8].
Nanotubes

Nanotubes are also one-dimensional objects, differing from nanofibers by the presence of an internal cavity, tens of nanometers in diameter. They have a finite length extending to several micrometres. The presence of a template is the necessary condition for the growth of nanotubes. Transmission electron microscopy is applied to examine and prove the nanotubular structure [32].

Colloidal particles

Colloidal particles are produced by the polymerization of aniline in the presence of suitable water-soluble polymers or nanoparticulate stabilizers [32]. They may have various shapes and sizes of 100-500 nm.

Other morphologies

A variety of additional morphologies, including flakes, ribbons or nanobelts are produced by tuning the pH profile during the oxidation of aniline [32]. PANI nanoneedles were obtained during interfacial polymerization when using a low concentration of reactants. Two-dimensional structures such as nanosheets or nanoplates have also been prepared. Many of these morphologies have been named after objects found in nature, for example, centipede-like, chrysanthemum-like, flower-like, lotus-leaf-like, rambutan-like, rose-like, sunflower-like or urchin-like, etc. [32]. Nature has thus always been a great inspiration to research.

1.6.5. Morphology studies

Scanning electron microscope

Scanning electron microscope (SEM) is the most widely used tool for investigating morphology. This is because of its versatility, its various modes of imaging, ease of sample preparation, as well as easy interpretation of the images. A very wide range of magnification is available which facilitates the visualization of virtually every
detail. In nanoscience and technology, this becomes an important characterization tool [54]. Surface structure and 3-D appearance of the sample is judged by SEM images. SEM studies are normally performed to examine the difference in surface morphology between the parent materials and their blends and composites [55]. SEM is helpful in determining whether the PANI component is homogeneously distributed throughout the matrix. Changes in structure and morphology can drastically affect the properties of conducting PANI, with profound implications for the material and its applications. The morphology of PANI changes during the protonation-deprotonation and oxidation-reduction processes.

**Transmission electron microscope**

Transmission electron microscope (TEM) is the most important characterization tool for a nanomaterial, because the particle size, morphology and inner structure are examined using TEM analysis [54]. Figure 1.7 illustrates the main thrust of the argument [56]. In addition to showing the shape of the object, TEM can reveal the microscopic structure and atomic composition using energy dispersive X-ray analysis. In TEM, it is important to study a large cross section of the sample, not merely one particle. This large area image gives the particle size distribution. Generally, a histogram of particle size distribution is plotted, which is more representative of the material synthesized. At higher magnifications, the lattice structure of individual nanoparticles is resolved.

**Atomic force microscopy**

Atomic force microscopy (AFM) technique is a very useful tool to study the changes occurring in morphology of electronic conductive polymers and non-conductive samples with high resolution. To study the morphology of PANI films, AFM *ex situ* experiments were carried out at room temperature. The noncontact mode was used for taking topographic images. Giz *et al* have studied the morphology of PANI doped with
Figure 1.7. The Multi-Layer Theory as a proposed framework for PANI nanostructure self-assembly. In each panel, the image on the left shows a schematic of the structure, while the paired image on the right shows the corresponding TEM observation [56].
different anionic surfactants and functionalized organic anions such as camphorsulphonate, methanosulphonate and trifluorsulphonate to correlate surface transformation changes of PANI with the chemical nature of the different anions [57]. Contractor group has studied the volume changes in islands, thin films, microtubules and nanowires of PANI by changing its electrochemical state in H\textsubscript{2}SO\textsubscript{4} and HCl as electrolytes using electrochemical AFM [58].

1.6.6. Thermal studies-TGA

The thermogravimetric analysis (TGA) technique is highly useful for evaluating the onset of thermal decomposition temperature and determining thermal stability of conducting polymers. The TGA results obtained for PANI show that the method of synthesis is important in determining the thermal stability of the polymer but the oxidation state of the polymer does not show any influence. The relative mass composition of polymeric materials is easily determined from the mass loss due to the volatilization of the conducting polymer component. The different stages of degradation are as follows: The first weight loss occurring from 30-200 °C is attributed to the expulsion of loosely-bound water and low-molecular weight oligomers [59]. The second weight loss taking place in the range of 200-300 °C is caused by the departure of physically-interacted acid dopant. The dopants that are bound to the imine centers of PANI are liberated in the temperature of 300-450 °C range. The final weight loss at 450-800 °C, corresponds to thermal decomposition of PANI backbone chains. Finally at more extreme temperatures the degradation of the polymer leads to production of gases such as acetylene and ammonia. In differential thermogravimetry (DTG) the actual measurement signal appears as derivative plot of the weight loss or gain. The thermal behavior of PANI thus shows a four-step weight loss process and is observed rather clearly in DTG curves.
1.7. Applications of polyaniline

PANI has many potential applications in multidisciplinary fields [60]. PANI being intrinsically conducting can be used for conductive adhesive, ink, paint, antistatic textile electrostatic discharge materials, etc. The viscosity of PANI dispersion under an electric field increases significantly. This property is useful for its application in electrorheological fluids. The ability of changing the electrical conductivity and color upon exposure to vapors finds its usefulness in the field of sensor, detector and indicator. The morphology changes during the protonation-deprotonation and oxidation-reduction processes and this property can be used as a membrane for gas separation, neutral solute separation and pH switching actuator. PANI shows very high dielectric constant, which makes it useful as capacitors and energy storage devices. PANI can be converted from conducting to an insulating material by dedoping process and this property is useful for the fabrication of memory devices. The strain is changed under a pulsed current. This property is important in artificial muscle application. PANI has the ability to accumulate and transform energy; hence, this ability of PANI allows it to be used as an electrode in rechargeable batteries, electrochromic displays, photovoltaic cells, transistors, as a medium for photoelectric devices, as electro-membranes, etc. Under various excitations PANI emits color and this phenomenon is applied in the fabrication of organic light emitting diodes. PANI coatings can provide significant corrosion protection to steel, copper and iron when exposed to corrosive environments. Investigation also showed that PANI has potential applications as electrochemical sensors, catalysts, metallization of printed circuit boards, antioxidant, etc. Some of the most important potential applications are briefly mentioned here and the Chart 1.2 illustrates the collective representation of all the possible applications.
Chart 1.2. Applications of polyaniline.
References


