SYNTHESIS

2.0 Introduction

Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 100 S/cm, many orders of magnitude higher than that of common polymers (<10^{-9} S/cm) but lower than that of typical metals (>10^{4} S/cm). Protonated PANI, (e.g., PANI hydrochloride) converts to a non-conducting blue emeraldine base when treated with ammonium hydroxide [1–4] figure 2.1

![Chemical structure of Polyaniline (emeraldine) salt and base](image)

**Figure-2.1** Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. “A” is an arbitrary anion, e.g., chloride.

The changes in physicochemical properties of PANI occurring in the response to various external stimuli are used in various applications [5, 6], e.g., in organic electrodes, sensors, and actuators [7–9]. Other uses are based on the combination of
electrical properties typical of semiconductors with materials parameters characteristic of polymers, like the development of “plastic” microelectronics [10], electrochromic devices [11], tailor-made composite systems [12, 13], and “smart” fabrics [14]. The establishment of the physical properties of PANI reflecting the conditions of preparation is thus of fundamental importance.

The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the syntheses of PANI; the resulting PANI, protonated with various acids, differs in solubility, conductivity and stability. For the present study, we have selected hydrochloric acid in equimolar proportion to aniline, i.e., aniline hydrochloride was used as a monomer. The handling of solid aniline salt is preferred to liquid aniline from the point of view of toxic hazards. Peroxydisulfate is the most commonly used oxidant and its ammonium salt was preferred to the potassium counterpart because of its better solubility in water. The concentration of aniline hydrochloride was set to 0.2 M. various oxidant/ monomer ratios have been used in the literature. To minimize the presence of residual aniline and to obtain the best yield of PANI, the stoichiometric aniline / peroxydisulfate ratio1:2 is recommended [15] figure 2.2. The polymerization is completed within 1 h at 0–2 °C [16]. The oxidation of aniline is exothermic so the temperature of the reaction mixture can be used to monitor the progress of reaction [17, 18]. Temperature profile is well reproducible.
2.1 Synthesis of polyaniline by various techniques

Different synthesis used to produce PANI including chemical, electrochemical, enzymatic, plasma, photo and numbers of other special methods. Chemical polymerization is again subdivided into heterophase solution, interfacial, seeding, metathesis, self-assembling and sonochemical polymerization, etc.

2.1.1 Heterophase polymerization

The heterophase polymerization technique includes different methods of polymerization such as precipitation, suspension, microsuspension, emulsion, miniemulsion, microemulsion, dispersion, reverse micelle and inverse polymerizations. In the case of suspension, microsuspension, miniemulsion and microemulsion polymerization methods the monomer should be sparingly soluble in water (as it has to form a separate phase) and form spherical droplets whose size is controlled by a proper choice of the dispersing technique (such as stirring, ultrasonic treatment or homogenization). These droplets are stabilized in an aqueous media through the addition of a surface active agent (stabilizer). The size of the droplets

\[
4 \, n \, \text{NH}_2\text{HCl} + 5 \, n \, (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \]

\[
\begin{align*}
\text{NH} & \quad \text{Cl}^- \quad \text{NH} \\
\text{Cl}^- & \quad \text{NH} \\
\text{Cl}^- & \quad \text{NH}
\end{align*}
\]

+ 2 \, n \, \text{HCl} + 5 \, n \, \text{H}_2\text{SO}_4 + 5 \, n \, (\text{NH}_4)_2\text{SO}_4

Figure-2.2 Oxidation of aniline hydrochloride with ammonium peroxydisulfate yields polyaniline (emeraldine) hydrochloride
Synthesis.......

varies, according to the polymerization method, in the following order: suspension >microsuspension >miniemulsion >microemulsion. The polymerization recipes are designed in such a way that the initiator should be soluble in the monomer instead of continuous phase and the polymerization should take place mainly inside the preformed monomer droplets. In this technique, the stabilizer must support the emulsification process and the stabilization of the monomer droplets, whereas in case of emulsion polymerization requires a separate free monomer phase. The emulsions are divided into two types: “direct”, oil in water (o/w); and “inverse”, water in oil (w/o). The selection depends on the chosen emulsifier, the water to oil ratio, and the temperature of the polymerization. The microemulsion again is subdivided into general microemulsion and miniemulsion depending upon the droplet size and stability and the amount of surfactant used. To prepare macroemulsion and miniemulsion, a degree of shear force is required, whereas the microemulsion is formed spontaneously [19].

2.1.2 Synthesis of polyaniline colloidal dispersion

PANI is typically produced by the oxidative polymerization of aniline in an acidic aqueous medium and is obtained as a precipitate [20, 21]. If a suitable water-soluble polymer such as poly (N-vinylpyrrolidone) (PVP) is added to the reaction mixture, colloidal PANI particles are formed instead of precipitation. Such a process is known as dispersion polymerization [22]. In this process: (a) the monomer is soluble in the reaction medium; (b) the produced polymer is insoluble under the same conditions; and (c) its macroscopic precipitation is prevented by the presence of the so-called steric stabilizer. Hence, such colloids are called dispersions. The colloidal PANI particles have a typical average size of a few tens to hundreds of nanometers
and are thus often regarded as nanocolloids. The shape of the particles may be spherical, globular, granular, cylindrical or branched dendritic structures [23, 24].

2.1.3 Direct and inverse emulsion polymerization of aniline

In the direct emulsion polymerization the monomer is dispersed in an aqueous phase to form a uniform emulsion. The emulsion is stabilized by a surfactant and the polymerization reaction is carried out [25]. For the synthesis of PANI by emulsion polymerization, aniline along with a protonic acid and an oxidant are combined with a mixture of water and a nonpolar or weakly polar solvent, for example, xylene, chloroform, or toluene (sparsely soluble or insoluble in water). In some instances to form an emulsion with the above systems, a protonic acid such as dodecylbenzene sulfonic acid is employed, which has a substantial emulsifying ability in weakly polar solvents. In addition, the product of the above reaction cannot be isolated directly, since the 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 [26, 27]. The inverse emulsion polymerization process involves the formation of an aqueous solution of the monomer aniline which is emulsified in a nonpolar organic solvent. The polymerization is then initiated with an oil-soluble initiator such as ammonium persulfate (APS), benzoyl peroxide, and so on. The reaction carried out in such a heterogeneous phase has several distinct advantages compared to that of methods discussed earlier. The physical state of the inverse emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant here than those in bulk polymerization. The product of an emulsion polymerization can be used in many instances directly without
Synthesis.......

further separations. During the polymerization, both a high molecular weight and a high reaction rate can be simultaneously achieved. During the course of the reaction, PANI remains as a soluble component in the organic phase. At the end of polymerization the organic phase is separated and washed repeatedly with distilled water. The solution is then treated with anhydrous sodium sulfate or other suitable chemicals 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 the PANI salt [28, 29].

2.1.4 Reversed micelle polymerization of aniline

A transparent and homogeneous reversed micelle solution is prepared by dissolving the dodecyl benzene sulfonic acid (DBSA) and an aqueous APS solution in the isooctane through vigorous stirring (A). The aniline is dissolved in isooctane in order to form a homogeneous solution (B); the ethanol is added to this system with thorough stirring. The reaction is initiated through the drop-wise addition of solution (B) into the reversed micelle solution (A). At the end of the reaction a dark green colored DBSA-PANI suspension is obtained. The suspended precipitate is then filtered, followed by washing with methanol and deionized water to remove impurities such as APS, free DBSA and unreacted aniline. The washing is continued until the pH value of the washed liquid reaches pH 7.0. The PANI obtained from reversed micelle polymerization has better conductivity, processability, crystallizability, electrochemical activity, solubility, thermal stability and higher molecular weight compared to the products obtained from other processes. The particles of the DBSA-PANI synthesized through the reversed micelle process can attain a size within the nanoscale, with a needle-like shape [30].
2.1.5 Solution polymerization of aniline

PANI has also been synthesized by solution polymerization of aniline. Aniline has been polymerized in chloroform as a solvent and electro-polymerized in acrylonitrile solvent. Generally the processability of PANI is very poor due to its poor solubility in all available solvents. Therefore, the PANI prepared through a solution polymerization process has better processability since it is already in a solution [31].

2.1.6 Interfacial polymerization of aniline

When polymerization reaction is carried out in the interfaces of two immiscible solvents it is known as interfacial polymerization. PANI has been synthesized using a mixture of two immiscible solvents such as water and chloroform in the presence of different acids acting as dopants. The reaction is initiated by an oxidizing agent such as APS, \( \text{H}_2\text{O}_2 \), and so on at room temperature or at any preferable temperature in the presence or absence of a surfactant. The final product is isolated by centrifugation. Various products ranging from a one-dimensional radially aligned nanofiber to a spherical shaped PANI with a narrow size distribution can be obtained using this method, through the correct selection of suitable reaction parameters and reagents [32]. Chen et al. prepared different shaped PANI through the interfacial polymerization method by simply varying aniline (monomer) to salicylic acid SA (dopant) at different ratios [33]. (a) When the concentration ratio of (SA) to (aniline) is 1:10, fine nanorods are obtained. (b) When this ratio is 5:10 spherical PANI particles are obtained. (c) When this ratio is 9:10, a bud-like structure is obtained.
2.1.7 Self-assembling polymerization

The PANI thin films are directly grown on the polymeric film substrates by polymerizing aniline monomer in a vapor-phase. The 10 wt% solution containing FeCl$_3$, camphor sulfonic acid and Fe [p-toluene sulfonate]$\_3$ is prepared in methyl alcohol (MeOH) and coated on a clean polymeric substrate film such as polyethylene terephthalate (PET), polyimide (PI), polyvinyl chloride (PVC), polystyrene (PS), and so on by a dip or spin coating technique and is then dried. The dry coated film is exposed to aniline vapor for 5–60 min in a closed reaction chamber under different temperatures. At the end of the polymerization reaction, the PANI films that have grown on the substrate are washed with methanol several times to remove unreacted oxidant, aniline monomer and any by-products (e.g. FeCl$_2$) and are then dried for 3 min at 80 $^\circ$C. Zhang and Wan synthesized a PANI nanotube with an 80–200 nm outer diameter and a 20–40 nm inner diameter by the self-assembled method [34].

2.1.8 Electrochemical synthesis of polyaniline

At present there is a twofold interest in the electrochemical polymerization (ECP) process. Firstly, the ECP reaction provides a better method of polymerization with a fine control of the initiation and termination steps. Secondly, ECP has a degree of technological potential. The electrochemical reactions are often much cleaner and the PANI obtained is expected to be in a relatively purer form (as no additional chemicals such as surfactant, oxidant, and so on are used here) compared to that obtained from chemical polymerization. Furthermore, the use of limited chemicals reduces the problem of pollution. Electrochemical methods are generally employed for the polymerization of aniline under: (i) a constant current (galvanostatic) (ii) a constant potential (potentiostatic) and (iii) a potential scanning/cycling or sweeping.
The first method essentially consists of a two-electrode assembly dipped in an electrolyte solution containing the monomer, and a specified level of current is passed to form PANI film on the surface of a platinum foil electrode. The polymerization of aniline at a constant potential produces polymer powder which adheres weakly on the electrode [35]. On the other hand, the electro-oxidation of aniline by continuous cycling between the predetermined potentials produces an even polymeric film which firmly adheres on the electrode surface [36]. This thin film of PANI can then either be reduced or oxidized to control conductivity. Even thicker film can be produced and peeled off from the electrode surface to yield a free-standing, electrically conducting film. Fine nanowires can also be prepared by ECP using a template, which is discussed in the section of template synthesis. Though the usual anode material would be platinum or conducting glass, many metals such as Fe, Cu, Au, graphite, vitreous carbon and stainless steel have been used. Gupta and Miura synthesized PANI nanowires by electropolymerization on a stainless steel electrode at the potential of 0.75V vs. SCE [37].

2.1.9 Enzymatic synthesis of polyaniline

Horseradish peroxidase (HRP) and soybean peroxidase (SBP) are oxidoreductase enzymes capable of oxidizing aromatic amines in the presence of hydrogen peroxide. These enzymes can be derived from non-contaminant renewable sources and have high reaction selectivity to aromatic compounds and they cut down the oxidation byproducts to water. For these reasons, peroxidase catalyzed polymerization of aniline is considered to be an environmental friendly route to obtain PANI. Most of the research related to enzymatic polymerization of aniline was carried out using polyelectrolyte templates such as sulfonated polystyrene, poly (vinyl
Synthesis....
phosphonic acid) and deoxyribonucleic acid (DNA). These studies have shown that these templates provide a local environment, which promotes para-directed, head-to-tail coupling of aniline radicals. This poly anion-assisted polymerization allows the enzymatic syntheses for water-soluble complex of conducting PANI with a well-defined structure at a pH level as high as 4.3. However, the high degree of complexity between PANI and the poly anion renders it difficult to obtain bulk PANI that is required for specific applications, such as free standing films or fibers. Zemel and Quinn [38] have reported that bulk of electrically conductive PANI can be synthesized using HRP as a catalyst, in an aqueous media at pH 3.0. However, under such reaction conditions, the HRP goes through a rapid denaturing process. Thus, to carry out the reaction, a large amount of this enzyme is needed. The problem can be avoided by performing the reaction at a pH above 6.0 in an aqueous media. When the synthesis of PANI is carried out at a high pH in the absence of an anionic template, a non-conductive material is obtained. The lack of electrical conductivity is attributed to structural defects such as branched or cross-linked chains and phenyl–phenyl couplings, which causes a loss of electronic conjugation of the PANI backbone. SBP is an enzyme with a higher thermodynamic stability than HRP and a better catalytic activity under an acidic environment [39]. SBP may therefore be used to produce conductive PANI without the use of a template.

2.1.10 Photo-induced polymerization of aniline

The photo-induced polymerization of aniline involves the photo-excitation of aniline monomer to obtain polyaniline. Polyaniline has been synthesized by using Nd: YAG laser to irradiate an Au electrode in a solution containing aniline under an applied external bias. Only photons in the UV or visible region are also used to induce polymerization of aniline in an aqueous solution of transition metal salts. The photo-
Synthesis......

polymerization methods yield a composite material where silver nanowires and microwires are formed along with polyaniline. The morphology of the conducting polymer is strongly dependent on the excitation wavelength. A more globular morphology is observed for the UV synthesis, whereas a more fibrillar morphology is detected for the visible light synthesis [40].

2.1.11 Chemical Synthesis of Emeraldine Salt

The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulfate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equimolar volumes of aniline and hydrochloric acid) was dissolved in distilled water in a volumetric flask to 100 ml of solution. Ammonium peroxydisulfate (0.25M) was dissolved in water to 100 ml of solution. Both solutions were kept for 1 hour at room temperature (25°C), then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the polyaniline precipitate was collected on a filter, washed with 300 ml of 0.2 M HCl, and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then in vacuum at 60°C. Polyanilines prepared under these reaction and processing conditions are further referred to as “standard” samples. Additional polymerizations were carried out in an ice bath at 0–2°C. The acidity of the reaction mixture was increased by replacing 10 ml of water with 10 ml of 2 M HCl [41].

2.2 Synthesis of Polyaniline and its Composites

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ((NH₄)₂S₂O₈),
Hydrochloric acid (HCl), Zinc ferrite (ZnFe\textsubscript{2}O\textsubscript{4}), Nickel zinc oxide (NiZnO\textsubscript{3}) and Copper oxide (CuO) were procured from sigma and were used as received.

2.2.1 Synthesis of Polyaniline / ZnFe\textsubscript{2}O\textsubscript{4} Composites

0.1 mole aniline monomer is dissolved in 1 mole hydrochloric acid to form polyaniline hydrochloride. Fine graded pre-sintered ZnFe\textsubscript{2}O\textsubscript{4} (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40 and 50 is added to the polymerization mixture with vigorous stirring in order to keep the ZnFe\textsubscript{2}O\textsubscript{4} powder suspended in the solution. To this reaction mixture, APS as an oxidant is added slowly with continuous stirring for the period of 1 hrs at temperature 2\textsuperscript{0}C. Polymerization of aniline takes place over fine grade zinc ferrite particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60\textsuperscript{0}C for 24 hrs to get resulting composites [42]. In this way five different polyaniline/ ZnFe\textsubscript{2}O\textsubscript{4} composites with different weight percentage of zinc ferrite (10, 20, 30, 40 and 50) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium.

2.2.2 Synthesis of Polyaniline/Ni ZnO\textsubscript{3} Composites

Polyaniline and Polyaniline/NiZnO\textsubscript{3} composites are prepared by oxidative polymerization method. The equimolar volume of aniline and hydrochloric acid is mixed and stirred for 1hr to form aniline hydrochloride. Fine graded pre-sintered NiZnO\textsubscript{3}(AR grade, Fine Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40 and 50) is added to the polymerization mixture with vigorous stirring in order to keep the NiZnO\textsubscript{3} powder suspended in the solution. To this reaction mixture,
Synthesis....... 

\[ (NH_4)_2S_2O_8 \] used as an oxidant, is added slowly drop-wise with continuous stirring for the period of 1 hrs at temperature 2^0C. Polymerization of aniline takes place over fine grade Nickel zinc oxide particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60^0C for 24 hrs to get resulting composites [43]. In these way five different Polyaniline/Ni ZnO\textsubscript{3} composites with different weight percentage of Nickel zinc oxides (10, 20, 30, 40 and 50 wt. %) in Polyaniline has been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium.

2.2.3 Synthesis of Polyaniline – CuO Composites

0.1 mol of aniline was dissolved in 1 M HCl to form aniline hydrochloride. Copper oxide is added in the weight percent of 10, 20, 30, 40 and 50 to aniline hydrochloride solution with vigorous stirring in order to keep the tantalum pentaoxide suspended in the solution. To this reaction mixture, 0.1 M of ammonium persulphate \[(NH_4)_2S_2O_8\] which acts as the oxidant was added slowly with continuous stirring for 1 hours at 2^0 C. The precipitated powder recovered was vacuum filtered and washed with water and acetone. Finally the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In this way 5 different Polyaniline / CuO composites with different wt % of CuO (10, 20, 30, 40 and 50) in polyaniline have been synthesized [44]. All the composites so obtained above are crushed into fine powder in an agate mortar in the presence of acetone medium.

The powders of polyaniline, polyaniline – ZnFe\textsubscript{2}O\textsubscript{4}, polyaniline – Ni ZnO\textsubscript{3} and polyaniline – CuO composites so obtained from synthesis techniques discussed in
Synthesis......
the early sections are crushed and ground finely in the presence of acetone medium in
agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness
which varies from 1 to 2 mm by applying pressure of 90 MPa in a hydraulic press.
The pellets of polyaniline and its composites so obtained from above mentioned
techniques are coated with silver paste on either side of the surfaces. The copper
electrodes are placed on each of the surface to obtain better contacts.
REFERENCES


