Chapter - II

2. Synthesis

The polyacetylene metallic properties was initially reported by Heeger, MacDiarmid, Shirakawa, and their co-workers, which open up the another new field of polymer i.e. conducting polymeric materials and has gained lot of interest among scientific community. Conducting polymers have many potential significance over traditional metallic conductors due to its conducting inherent properties of a conjugated polymer. Since polyaniline was included in the field of intrinsically conducting polymeric materials, has been the important candidate for engineering applications. The great effort has been involved in preparation of high conducting polyaniline with easy processing methodologies by doping organic and inorganic compounds [1-3].

2.1. Introduction

Polyaniline can be prepared by either chemical or electrochemical oxidative polymerizations of aniline using hydrochloric acid which acts as protonator and ammonium persulphate acts as initiator. [4]. The polyaniline also have been developed by metal catalyzed processes and used for many electrochemical device applications.

2.1.1 Chemical Synthesis of Polyaniline

The polymerization of aniline was done by chemical oxidation method using hydrochloric acid (HCl) as a protonator and an oxidant such as ammonium persulphate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) with lithium chloride (LiCl) at 0 – 5 °C [5]. As the polymerization proceeds, aniline undergo oxidation to form a polyaniline (PANI) precipitates out as the emeraldine salt which can be convert into the emeraldine base form by
treated with a base such as ammonium hydroxide (NH$_3$OH). The properties of PANI depends on the
type of acid used, molar concentration of acid, oxidant ratio, temperature, reaction time and neutral
salts present in the final compound [6]. Molecular weights of traditional synthesized polyaniline can be
vary from $M_w = 50,000$ to $M_w = 385,000$ for this chemical oxidation polymerization.

2.1.2 Electrochemical Synthesis of Polyaniline

The electrochemical oxidation polymerization of aniline is carried out either by constant potential or
current, potential scanning or cycling methods. In general, the electrochemical polymerizations take
place in inert electrode in presence of aniline as an electrolytic solution. By this method easily we can
control the electrochemical stoichiometry and the polymerization initiation and termination steps [7].
The resulting polyaniline is highly influenced by the preparation conditions used during polymerization.

2.1.3 Metal Catalyzed Synthesis of Polyaniline

It is found difficult to prepare the meta-substituted or ortho-substituted aniline derivate due to the
steric effects. However, the chemical and electrochemical oxidative polymerizations techniques are
useful to prepare the para-substituted polyaniline derivate [8]. The meta-substituted polyaniline
derivate can be by metal catalyzed C-N bond reactions which offer an avenue to study ortho-polyaniline
derivatives [8]. There are two primary metal catalyzed couplings such as the palladium of aryl halides
and Ullmann-Goldberg for aryl amines and will be function as our primary synthetic methods.

The meta – polyaniline derivate was prepared by using the Ullmann-Goldberg copper mediated coupling
[9 – 12] and synthesized meta-para-oligoanilines [13, 14] for organoferromagnetic purposes. The
reaction conditions for an Ullmann-Goldberg copper reaction involve copper (I) iodide as copper
source and potassium carbonate as an inorganic base at 150 °C for 48 h. Recently, it is also discovered that additives of amino acids and alkyl diamines promote coupling by Buchwald, Ma, and co-workers [15 -17]. However, a drawback in to the Ullmann-Goldberg copper coupling is that the allowed radical coupling is uncontrollable and produces largely insoluble materials due to cross linking.

2.2 Methods of Synthesis

Polyaniline have been prepared by chemical oxidation method of aniline monomer in the presence of 1M HCl [18]. The prepared conducting polymer is called an emeraldine salt. For chemical synthesis, there are many different oxidizing agents such as potassium permanganate, ammonium peroxydisulfate [19], hydrogen peroxide [20], ferric chloride [21] and citric nitrate and sulfate [22]. Typically the ratio of aniline to oxidizing species has been reported to be oxidant/aniline 1.25 (a stoichiometric equivalent of oxidant) and other chemical polymerization shows a stoichiometric deficiency of the oxidant with respect to aniline (oxidant/aniline ratio »0.25) [23, 24].

The synthesis have been carried out by mixing aniline hydrochloride and ammonium persulphate at 0 – 5 °C, followed by the separation of precipitate PANI hydrochloride using vacuum filtration and drying at 50 °C for 12 hr to achieve constant weight [25]. Aniline hydrochloride was dissolved in distilled water in a 100 ml volumetric flask and ammonium persulphate (APS) (0.25M) was dissolved in water also to 100 ml of solution [26]. Both solutions were kept for 1 hour at 5 °C, then mixed in a beaker with continuous stirring with a magnetic stirrer and left at rest to polymerize for 24 hr. Next day, the polyaniline precipitate was collected on a filter, washed with 300 ml portions of 0.2 M HCl in order to remove the excess monomers and followed by distilled water and acetone to remove APS salts and oligomers. Polyaniline hydrochloride powder was dried under dynamic vacuum at 50 °C. The prepared polyaniline under above reaction conditions are referred as “standard” samples. [27 - 29].
2.2.1 Polymerization Mechanism

Polyaniline (PANI) prepared by electrochemically or chemically, it generally owes that there is a similar polymerization mechanism. In both the cases, the polymerization process takes place via the following mechanism:

In the first step, radical cation is form by an electron transition from the aniline nitrogen atom of the 2s energy level as shown in Figure 2.1

![Figure 2.1: The formation of the aniline radical cation and its different resonant Structures](image)

The radical cation of aniline formed has several resonant forms, in which the third form of radical cation is more reactive due to its inductive effect without any steric phenomenon in the aromatic ring.

The next step followed to the formation of dimer by “head-to-tail” reaction between the radical cation with the third form of aniline radical cations in acidic medium. Further, the dimer undergo oxidation to form a new radical of cationic dimer, as shown in Figure 2.2:
Later, the formed radical cation dimmer reacts either with another dimmer or with the radical cation monomer respectively to form a trimer or a tetramer. The similar above steps continue results the formation of the polyaniline (PANI) as shown in Figure 2.3.
2.2.2 Materials used for composites preparation

All the analytical grades chemicals were used for the preparation of polyaniline and its composites. Aniline (purity 99.99%), Ammonium persulphate (NH$_4$)$_2$S$_2$O$_8$; (APS), Hydrochloric acid (HCl), Zinc ferrite (ZnFe$_2$O$_4$) and Nickel ferrite (NiFe$_2$O$_4$) were purchased from Sigma-Aldrich, India.

2.2.3 Synthesis of ZnFe$_2$O$_4$ nanoparticles

ZnFe$_2$O$_4$ nanoparticles are prepared by, known quantity of zinc salt and iron salt were dissolved in minimum amount of water and similarly oxalic acid was dissolved in water in a separate container. These two solutions were mixed well to form a metal oxalate a precipitate. The precipitate was filtered through sintered glass and washed with double distilled water. Finally, washed with dry acetone and dried under vacuum [30 -32]. Metal oxalate mixture is grounded well with polyvinyl alcohol in 1:5 in a pestle and mortar. The reaction was transferred into crucible and initially it was burnt in an electrical oven for complete combustion of the fumes. The resultant residue was transferred into microwave oven for complete combustion process. The reaction was completed within 10 minutes at high power level to form nanosized ZnFe$_2$O$_4$ particles. On cooling to room temperature treating with acetone separates carbon impurity [33].

2.2.4 Synthesis of PANI/ZnFe$_2$O$_4$ nanocomposites

The PANI/ZnFe$_2$O$_4$ nanocomposites were prepared by an interfacial polymerization method with different weight percentage of ZnFe$_2$O$_4$ (10, 30 & 50 wt %). One gram of aniline was dissolved in 40 ml of CHCl$_3$. 0.1M ammonium persulfate was dissolved in 1M HCl and the ZnFe$_2$O$_4$ nanoparticles are added to
the above mixture of aqueous and organic phase. After 5 minutes dark green precipitate formed slowly at the interface and then gradually diffused into aqueous phase. After 24 hours, the entire aqueous phase was filled homogeneously with dark green colour film [34], organic layer observed shows orange colour due to the formation of aniline oligomers. The aqueous phase was then collected and washed with ethanol and water to remove the unreacted aniline. The residue of polymer thus obtained is purified and dried in vacuum oven at 40°C for 24 hr [35]. The dried polymer composite sample was used for structural characterization and further used to study the electrical and magnetic properties.

2.2.5 Synthesis of NiFe$_2$O$_4$ nanoparticles

Pure NiFe$_2$O$_4$ nanoparticles were prepared by chemical co-precipitation method in air atmosphere using EDTA as stabilizing agent. In a typical procedure, 0.5M of nickel nitrate and ferric chloride were dissolved in 50 ml of distilled water-ethanol (equal volume) and stirred for 10 min at 80 °C in a round bottom flask, as a sulfur source 0.5 M Na$_2$S.9H$_2$O was dissolved in 50 ml of distilled water-ethanol which was added drop wise to the above solution and stirrer for 15 min. As a result the color of the solution changes to yellow [36]. Then 50 ml of ethanol was added to above solution under stirring followed by the addition of 1 gram EDTA of 10 ml solution drop by drop and the resulted solution was stirred for 2 hours at 80 °C [37]. The solution was cooled at room temperature and the resulting precipitate was centrifuged. The obtained dispersions were washed several times by distilled water and alcohol to remove the impurities, including traces of EDTA and the original reactants. Finally the wet precipitate was dried in hot air oven at 80 °C for 24 hr.

2.2.6 Synthesis of PANI - NiFe$_2$O$_4$ nanocomposites

Aniline (AR grade) was purified by distillation before use and ammonium per sulphate [(NH$_4$)$_2$S$_2$O$_8$], HCl were used as received. 0.1 mole aniline monomer is dissolved in 1 mole
hydrochloric acid to form polyaniline. Fine graded pre-sintered nickel ferrite (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 5, 10, 15, 20 and 25 is added to the polymerization mixture with vigorous stirring in order to keep the nickel ferrite powder suspended in the solution. To this reaction mixture, \([(NH_4)_2S_2O_8]\) which is used as an oxidant is added slowly drop-wise with continuous vigorous stirring for the period of 4-6 hours at temperature 0-5°C. Polymerization of aniline takes place over fine grade NiFe$_2$O$_4$ 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 60-80°C for 24 hrs to get resulting composites. In this way, five different polyaniline - NiFe$_2$O$_4$ composites with different weight percentage of nickel ferrite (5, 10, 15, 20 and 25) in polyaniline have been synthesized [38]. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium.

2.3 Preparation of pellets

The 10 mm diameter pellets was prepared by applying 10 Tons with thickness of 1 mm using a UTM – 40 (40 Ton Universal testing machine). For temperature dependent conductivity and sensor studies, the pellets are coated with silver paste on either side of the pellets to obtain better contacts [39].
Reference


