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Synthesis and applications of polyaniline as one of the most explored conducting polymer

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Abstract
Polyaniline has received much attention among conductive polymers, and extensive research has been done on it in both its native and functionalized forms. This is due to the ease with which polyaniline and its composites can be made. Polyaniline is considered as one of the most explored conducting polymer due to is unique properties. This article explains the methods of synthesis of polyaniline and also focuses the various applications of polyanilines in the field of conducting polymer.

Keywords: Conducting polymer, polyaniline (PANI), synthesis, biomedical application

1. Introduction

Among conducting polymers, polyaniline (PANI) is unique for its extraordinary ability to conduct electricity, biocompatibility, and low toxicity. Polyaniline is the most promising and most explored among conducting polymers, and polyaniline has high stability, high processability, tunable conducting and optical properties. The conductivity of polyaniline is dependent upon the dopant concentration, and it gives metal-like conductivity only when the pH is less than 3 [1]. Polyaniline exists in different forms (Figure 1). They are classified as leucoemeraldine, emeraldine, and pernigraniline, by their oxidation state, i.e., leucoemeraldine exists in a sufficiently reduced state, and pernigraniline exists in a fully oxidized state. Polyaniline becomes conductive only when it is in a moderately oxidized state and acts as an insulator in a fully oxidized state [2].

2. Synthesis of Polyaniline: The polymer backbone consists of both quinoid and benzoid rings, in differing proportions. The difference in the ratio causes the existence of three oxidized states: the fully reduced leucoemeraldine form is in a quinoid state, the fully oxidized pernigraniline form is in a benzoid state and the conductive emeraldine form has an equal ratio of both benzoid and quinoid rings. The dopant does not change its chemical property and will not create any bond with the main chain; it exists in the close vicinity of the polymer chain [3].
The chemical oxidation method is one of the most straightforward methods to synthesize polyaniline; in this method a monomer precursor of the corresponding polymer is mixed with an oxidizing agent in the presence of a suitable acid under ambient conditions to give products, where the doping acid and oxidizing agent are those preferred by the authors concerned (Scheme 1). The change in color of the reaction medium to green indicates the formation of polyaniline. The preparation of the composite also follows the same method. Generally, oxidizing agents like ammonium persulfate, ammonium peroxy disulfate, ceric nitrate, ceric sulfate, potassium bichromate, etc. are used. Depending upon the pH of of acid dopant, the conductivity effectively modulates the physical parameters. The polymer and composite possess good conductivity when the pH is between 1 and 3 [4, 6].

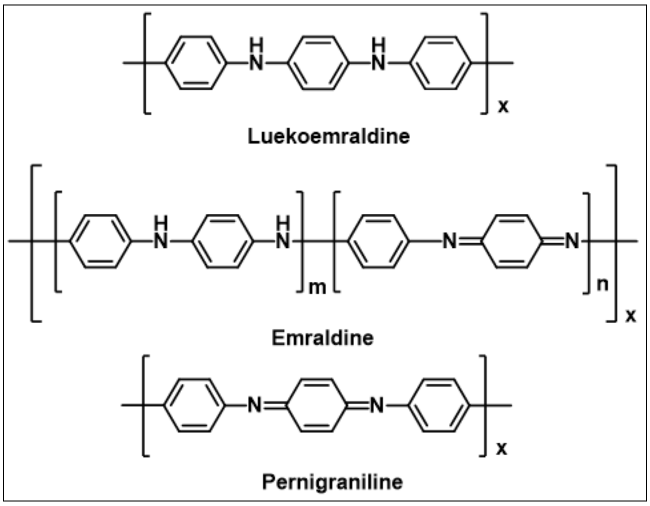
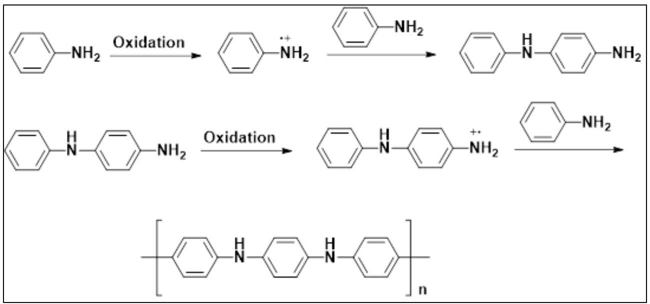


Fig 1: Structures of various forms of polyaniline



Scheme 1: Synthesis of polyaniline by the chemical oxidation method

Interfacial polymerization is also used to synthesize polyaniline, in which an aniline monomer is solubilized in an organic solvent like toluene, an oxidant solution and a dopant acid-containing aqueous solution. A microemulsion technique is also followed for the synthesis of polyaniline, where the polymerization also takes place in the interface between two immiscible liquids, but the difference is in the surfactant used [7, 9]. The electropolymerization technique happens without the effect of an oxidant, and is the same in the case of polyacetylene [10, 11]. Electrospinning is also used to synthesise fibrous polymer morphologies of nano or micro diameters under the influence of a strong electrical field. In this case, a high voltage is applied to the polymer droplets, and the charged droplets get stretched due to surface tension, and at a critical point, the liquid erupts and starts to weave on the counter surface. The principles of both electrospraying and electrospinning are the same. Electrospinning is the only method to produce bulk polymer fibrous structure. Conducting polymers and their composites like pure polyaniline, polypyrrole, polyaniline/polyethylene oxide/carbon nanotubes have been prepared by this technique. There are lot of factors dependent on electrospinning, such as the molecular weight of the polymer, viscosity, distance between spinneret and counter surface, temperature, humidity, etc [12, 14].

3. Biomedical applications of Polyaniline (PANI)
The biocompatibility, biodegradability, and antiproliferative power of the polyaniline against pathogenic bacteria, as well as its conjugation capacity with biologically active molecules, have led to its use in the biomedical field [15, 16].

3.1 In Drug delivery: PANI is a promising photothermal converting material, and in the last years, numerous research groups have focused their work on this application. An accurately controlled delivery of cisplatin was recently investigated by You *et al*. developing PANI mediated polymeric nanoparticles modified by trastuzumab that guarantees cellular uptake due to its high affinity for tumor cells [17]. The composites were prepared by a twosteps procedure based on the first synthesis of Pt-loaded nanoparticles followed by a second nanoparticle modification by trastuzumab.

3.2 In Cancer Therapy: Besides the ability to work as drug carriers, PANI based materials have shown outstanding potential in cancer therapy.
Gd(III)-modified PANI particles were successfully realized by Lee *et al*. for simultaneous diagnostic imaging and localized photothermal therapy [18]. Gd/PANI nanocomposites were prepared by a two steps process. During the first step, PANI was prepared by the traditional oxidative polymerization reaction. Then, the amine groups of the polymer were chemically conjugated with diethylenetriaminepentaacetic dianhydride (DTPA-DA) to chelate and reduce the potential toxicity of Gd(III). The loading of Gd (III) on the modified PANI particles was carried out by mixing $GdCl_3.6H_2O$ with the composite in N-methyl-pyrrolidinone. Finally, the hydrophilicity of the surface of the Gd/PANI material was improved by modified polyvinyl alcohol (PVA) that allowed the conjugation with cetuximab (CET), an anti-epidermal growth factor receptor, as a targeting moiety.

3.3 In biosensors: CPs work as transducers due to their extraordinary properties, such as electroconductivity, redox properties, biocompatibility, and great sensitivity. The recent work of Shoaie *et al*. exhaustively displays the state of the art of PANI and PANI composites applications in the field of biosensors [19].

4. Conclusion
This review presents the method and application of PANI in biomedical field. Because the chemical-physical characteristics of the polymer are strongly dependent on the synthetic procedure used for its fabrication, a large part has been dedicated to this aspect. Polyanilines conducting polymers, and their composits, should be explored more in biomedical field to serve society in better way.

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