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Review

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Synthesis, Properties, Nanocomposites, and Electrochemical Applications of Polyaniline: A Review

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Abstract

Polyaniline, also known as PANI, is a polymer in the that is becoming more significant for academics in the field of nanotechnology due to the potential uses it has in sensor technologies, optoelectronics, and photonics. PANI can be rapidly doped by a broad range of acids and dopants due to the ease with which it may be manufactured and its exceptional resilience in the natural environment. In this article, we will discuss the redox and antioxidant properties of several substances, as well as their resistance to corrosion and electricity, sensing capabilities, and magnetic properties. In order to do this, we looked at the properties of the conducting polymer PANI and have discussed them briefly. It has been shown that the circumstances under which PANI is polymerized do not need to be changed in any way for it to be useful in a wide variety of scientific and technical applications. Matrix synthesis, which is often performed using PANI, is the method of choice for the creation of composite materials that are both electroactive and conductive. This article provides a concise survey of the uses of PANI and related composites in the field of polymer electronics.

Keywords: Polyaniline (PANI), plastics, aniline, polymers, polyelectrolytes

INTRODUCTION

Different from other types of polymers, conducting polymers are able to conduct electrons under particular circumstances because they are made up of monomer units connected by conjugated chemical

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H. Singh, Gajanan C. Upadhye, Shalini Sharma, Sumanta Bhattacharya. Synthesis, Properties, Nanocomposites, and Electrochemical Applications of Polyaniline: A Review. Journal of Polymer & Composites. 2023; 11(Special Issue 3): S13–S20p. bonds. Due to their conductivity, low density, and simplicity of manufacturing, these polymers may one day replace metals and semiconductors in commercial applications. As a conducting polymer, polyaniline (PANI) stands out for its low-cost production and exceptional environmental resilience. The building blocks of PANI (Figure 1) are the reduced (y) and oxidized (1 - y) monomer units.



Figure 1. Monomer of aniline.

The polymer's redox state is defined by the value of y, which may take on any discrete value between 0 and 1. The emeraldine form of PANI occurs at y = 0.5, whereas pernigraniline and leucoemeraldine are found at y = 0 and 1, respectively [1]. In nature, pernigraniline and emeraldine may be found in a variety of ionic forms, including salts and bases as mentioned in Figure 2 [2, 3].



Figure 2. Salt and base forms of pernigraniline and emeraldine.

There are many different hues, stabilities, and conductivities of PANI to choose from. The absorption band of leucoemeraldine (in *N*-methyl pyrrolidone) is located at 343 nm [1]. Organic and inorganic acids protonate emeraldine base to make PANI emeraldine salt. This behavior is called doping. Acids and PANI in the emeraldine base generate polycations [4]. Protons favor nitrogen imine atoms. Positive charges on neighboring nitrogen atoms redistribute electron density, "unpairing" the lone-electron pair without changing the overall number of electrons [5]. Cation radical delocalization along a polymer's conjugation length causes electrical conductivity. As protonation rises, emeraldine PANI's electron conductivity increases by a factor of 10 from 0% to 20% [6]. This behavior is exclusive to PANI and cannot be seen in any other material. It is possible for PANI cation radicals to delocalize through intramolecular as well as intermolecular pathways. For electron transmission from one polymer chain to another, the conducting polymer chains in this case should be oriented in one direction [7].

USE OF POLYANILINE IN ORGANIC ELECTRONICS

PANI is a poor conductor and has limited usage in electronics and engineering since polymer chain formation happens at neutral pH and elevations exceeding 150°C. When a system is considered "closed," however, PANI may be used as an electrode. A fibrillar PANI rechargeable battery [8] with 280 (W h)/kg was produced. These current sources outperform commercial ones for specific energy. Each charge degrades batteries by 0.15% due to PANI degradation and zinc passivation. PANI-based batteries are environmentally friendly and easy to process. PANI composite materials are being used to make supercapacitors due to their high specific capacitance when charging. Graphene or carbon nanotubes enhance capacitance [9, 10]. PANI electrochemically deposited on steel and manganese oxide composite electrodes have high capacitance and charging cycles [11, 12].

Conducting polymer composites cannot build transistors due to charge carrier mobility and the grainboundary effect. Modern technologies may manufacture materials with high charge carrier mobility (up to 3 cm²/(Vs)) and on-current-to-off-current ratios (over 104) [13]. Organic field transistors were vacuum deposited from oligomeric PANI and fullerenes. Fullerene is deposited on an aluminum gate electrode after oligomeric PANI evaporates. The transistor's drain and source are the fullerene layer's vaporized aluminum. Organic field transistors' switch-on/switch-off current ratio is 500 but repeatable [14]. The conducting polymer's composition affects PANI-based polymer light-emitting diodes' performance. Due to a low-molecular-mass dopant, PANI is stable in organic solvents, although poly (3,4-ethylene dioxythiophene)-based organic semiconductors are more efficient [15]. PANI on tin fluoride replaces platinum in solar cell interior electrodes [15–17]. To increase photoelectric conversion coefficient to 7% (6% for platinum), metal is replaced with a conducting polymer. Graphite and PANI electrodes reduce solar battery prices without affecting performance [18], whereas nanostructured PANI boosts photoelectric cell efficiency to 11% [19].

POLYANILINE SYNTHESIS WITH TARGETED SUPRAMOLECULAR STRUCTURE AND PROPERTIES

Aniline is typically synthesized via chemical or electrochemical polymerization using dopants. Many different structural, morphological, and redox states of PANI may be achieved by varying the synthesis method, temperature, time, oxidant, dopant, solvent, applied voltage at the electrode, etc.

Electrochemical Polymerization

The electrochemical synthesis of PANI is often believed to be the purest method since it eliminates the requirement for purification steps such as solvent removal and monomer/initiator molecule separation. Electrodes made of inert conducting materials are used in aniline polymerization. Background electrolytes and an acid are typically present in aqueous solutions for aniline electrochemical polymerization [20]. Current density for aniline polymerization is capped at 10 mA/cm² [21] due to the galvanostatic regime. Aniline may be electrochemically polymerized to produce PANI with a wide range of properties and shapes. Electro-petrochemical production of PANI-based composite materials is used in rechargeable batteries [10, 11] and organic field transistors [22].

Chemical Polymerization

An aniline polymerization oxidant is ammonium persulfate [22]. This oxidant polymerizes *N*-methyl-2-vinylpyrrolidone with 90% yield, 1.2 S/cm conductivity, and 1.17 dL/g viscosity. Polymerizing aniline in an acidic medium with a pH of 3 using various acids or buffer solutions yields the emeraldine salt. The easiest way to make polymers with customizable physicochemical properties and supermolecular structures is to chemically synthesize PANI. Any substrate may get conductive polymer (matrix). Electrochemical synthesis benefits from the substrate's conductivity.

Matrix (Template) Polymerization

Matrix (template) polymerization [23–24] converts monomers or oligomers into micromolecular structures using macromolecular structural-chemical information. Data builds micromolecular structures. Template effects result from multiple monomer-template interactions during the template polyreaction (hydrogen bonds, Coulomb contacts, covalent bonds, hydrophobic interactions) [25–28]. Template polymerization affects polyreaction rates, daughter macromolecule composition, organization, degree of polymerization, and isomeric composition [29–33]. In PANI research, "template" might be the polymer coexisting with the monomer or a solid substrate with template effects. Inorganic hard templates interact with monomers to change process parameters and polymer form. Monomer-initiator solution and stiff template induce tetra-plate polymerization [34–36].

Aniline polymerization uses a stiff template like carbon nanotubes, graphite, or inorganic oxides to adsorb the radical monomer or cation on the matrix surface and polymerize. Inorganic templates may combine PANI's mechanical, electrochemical, and acid-base reactivity [37]. Amorphous carbon improves this technique, and the composite might be employed as an organic molecule indicator electrode [38]. It makes electrochromic glass, super capacitors, secondary cells, sensors, and anticorrosive coatings [39]. Aniline chemical polymerization oxidized hard templates such as carbon nanotubes and graphene and its derivatives, creating composite materials with high capacitance. prototypes. Aniline polymerizes around surfactant micelles following a first or second critical micelle concentration [40]. This polymerizes aniline monomers or cation radicals in surfactant micelles into

PANI (Figure 3). Micelles may dissolve aniline [37]. Micelle structure determines conductive polymer shape in both circumstances. PANI nanofibils with 60 to 90 nm diameters and 1-m lengths are produced by adding cetyltrimethylammonium bromide to ammonium persulfate-induced aniline polymerization [41]. Aniline chemical polymerization uses cationic surfactants, dopants, and structural agents. Naphthalene sulfonic acid may synthesize PANI nanotubes and nanofibrils with adjustable sizes [29]. PANI, which is soluble in organic solvents, may be synthesized using many reagents, including 4-dodecylbenzenesulfonic acid, sodium dodecyl sulfate, bis(ethylhexyl) sulfosuccinate, tetradecyltrimethylammonium bromide, and surfactants.



Figure 3. Polymerization of aniline.

Aniline Polymerization Molds

Schematics template polymerization may synthesize PANI with the desired form using macromolecular templates such polyanions that interact electrostatically with PANI and water-soluble polymers that create hydrogen bonds [37]. The polyelectrolyte template (a polyacid) stabilizes and dopes PANI particles in solution to generate a conductive water-soluble substance [38]. This model eliminates the high-molecular-mass dopant only during breakdown at increased temperatures, increasing thermal conductivity. Water-soluble polymers and low-molecular-mass acids may synthesize stable conducting dispersions from PANI. Ammonium persulfate oxidizes aniline during template polymerization [39]. Hemoglobin or peroxidases may also polymerize aniline with oxygen or hydrogen peroxide. Laccases oxidize substrates. Polymerization uses strong polyacids such poly(4styrenesulfonic acid) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid). Hydrogen-bonding polymers (dopants) and low-molecular-mass acids (templates) generate these structures. PANI, polyvinylpyridine, polyvinylpyrrolidone, polyacrylamide, and hydroxypropyl cellulose are such polymers. Template polymerization suits homogeneous and interfacial settings. Interfacial polymerization dissolves aniline in both the organic (polysalt) and aqueous (anionic surfactant) phases of a solution. PANI at the interface and PSS-PANI (poly (sodium 4-styrene sulfonate)) synergize to slowly diffuse into the liquid. The PANI-polyanion complex polymerizes into spherical particles or extended structures of aggregated particles [40]. PANI-PSS complex particle sizes depend on polyanion molecular mass and homogeneous template polymerization concentration. When molecular weight > 6800 PSS-Na is present, the interpolymer complex has a 2 to 3 nm particle diameter at [aniline] = [PSS-Na] 4.5×10^{-2} mol/L. If component concentration exceeds this threshold, fibrillar aggregates of 70 to

90 nm and 200–1 nm develop. Polymerized PSS-Na particles are 100 to 130 nm and may combine into smaller particles [42].

PANIs formed at low aniline concentrations $(4.5 \times 10^{-2} \text{ mol/L})$ in hydrogen-bonding polymers vary in shape and size depending on the polymer and dopant. Polyvinylpyrrolidone-hydrochloric acid aniline template polymerization yields 50 to 150 nm particles. Aniline polymerized with poly(vinyl alcohol) and hydrochloric acid forms 200 to 300-nm-wide PANI structures. Interpolymer complexes generate 300-nm particles when p-toluenesulfonic acid substitutes hydrochloric acid [43]. The reaction medium's polyelectrolyte-template-to-aniline ratio controls whether PANI-polyelectrolytes form nonstoichiometric water-soluble or phase-separable complexes [44]. The complex produces flakes at 4:1 aniline: PSS-Na. PANI's protonated quinonediimine nitrogen atoms neutralize template charges because its nitrogen-to-sulfur ratio is 2.3. Template synthesis complex conductivity is unaffected by polyacid type or concentration. Real-world polymer soft template composite materials may be adjusted. PANI-PSS fibrils may precipitate platinum and ruthenium for methanol oxidation [45].

Plastics

Polyethyleneterephthalate, polyethylene, polypropylene, polystyrene, and polyamide-6 films and membranes are moldable. Most composites use amorphous or partially crystalline polymers. For polymer composites, in situ polymerization extends a monomer's polymer matrix. Amorphous portions absorb organic molecules; hence highly crystalline polymers cannot absorb much. Membranes create PANI- and crystalline polymer-based composites from aniline polymerization in holes [46]. PANI without a polymer template has a different morphology. The former creates 60 to 100 nm spherical particles, whereas the latter produces fibrils up to 300 nm. Polymerization forms fibrils on the template surface after PANI fills all holes. Surface morphology was explored to discover how template type influences PANI and polyamides (PA) 6, 6.6, 11, and 10.10 composites. PANI makes 100 to 500 nm spherical particles without template. Composites act similarly. Poly(sulfonic acid)-based perfluorinated carbon membranes like Nafion® make soft templates [47]. The reaction vessel membrane separates aniline and ammonium persulfate (oxidant). Intercalated PANI polymerization yields PANI-Nafion®. Fuel cell membrane-electrode blocks use these catalytic and gas-diffusion composites [48]. PANI production employing films and membranes as polymeric templates combines polymer mechanical characteristics, PANI conductivity, pH sensitivity, and electrochemical activity. These materials form sensors and actuators for many applications [49–51].

CONCLUSION

Since the beginning of the 20th century, scientists have been able to synthesize PANI, which enables exact control over the structure and physicochemical properties of the compound. Production of PANI is profoundly influenced by organic electronics. PANI is used in the construction of switches, controllers, battery storage, and solar cells. It is possible that synthesizing a PANI will result in the development of composite materials that have superior mechanical and physicochemical characteristics of the template.

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