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Synthesis of Polypyrrole and Their Application

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Abstract

Recently, conductive polymers—in particular, polypyrrole (PPy)—have gained popularity for a wide range of industrial uses because of their superior environmental resilience, outstanding electrical conductivity, good thermal stability, and relative simplicity of synthesis. The presence of a conjugated electron or an alternating single- and double-bond system in the chemical structure of conductive polymers is generally what makes them conductive in nature. Because of this distinctive chemical property, conductive polymers have drawn the interest of numerous researchers and scientists from a variety of academic and industrial backgrounds worldwide. PPy has been synthesised and prepared by employing various techniques, such as electrochemical or chemical oxidation of pyrrole monomer in various organic solvents and in aqueous media. It has been actively used in many potential applications, such as electronic devices, sensors, batteries, microactuators, antielectrostatic coatings, and biomedical. The primary architectures, techniques of preparation, possible uses, and future directions of PPy are described in this overview. Processability, thermal stability, and conductivity are the primary attributes that need to be improved for further advanced applications because of the chemically manufactured PPy's wide variety of uses.

Keywords: Polypyrrole; Nanostructures; Synthetic methods; Properties; Applications

I. Introduction

Conventional polymer polymers are among the most widely used materials in the world today and have high insulating qualities. A. J. Heeger, A. J. MacDiarmid, and H. Shirakawa did, however, create a novel kind of polymer material in 1977. Polyacetylene doped with iodine showed a considerable improvement in conductivity, reaching 10^3 S cm^{-1} (Shirakawa et al., 1977). The creation of conductive polymers (CPs) was largely spurred by the discovery of a number of polymers with comparable properties, including polyaniline, polythiophene, and polypyrrole (Namsheer K and Rout, 2021). Pyrrole polymerization produces the organic polymer known as PPy. In 1968, it was proved to be a CP. Because of its more effective redox properties (Burroughes et al., 1990), stabilised oxidised form, ability to produce towering conductivity (Wise et al., 1998), water solubility, commercial accessibility, and valuable electrical and optical properties, PPy has been the subject of extensive research among the many CPs. For a century, pyrrole blacks were recognised when they were first produced as powders through the chemical polymerization of pyrrole. These enigmatic polymers have not been well described, however they are known to be pyrrole polymers mostly bonded by α,α' carbons. In 1963, Weiss and colleagues (McNeill et al., 1963) described how to pyrolyze tetraiodopyrrole to create unexpectedly conductive compounds. To investigate this system as a CP, free standing films with sufficiently good mechanical characteristics were created in 1979 using an enhanced electrochemical approach (Diaz et al., 1979). By oxidising pyrrole in sulfuric acid, Dall'Olio et al. (1968) produced PPY, a black powder with a room temperature conductivity of 8 Scm^{-1}. Later, IBM employees expanded on Dall'Olio's work by explaining that electrochemical polymerization can be used to create films of this polymer (Simonet and Raultberthelot, 1991). When these films are electrochemically cycled, their conductivity fluctuates between an insulating and conducting state by 100–200 S cm^{-1} (Kanazawa et al., 1979).

SYNTHESIS OF POLYPYRROLE

In addition to its high stability, improved conductivity, and relative simplicity of homopolymer and composite formation, polypyrrole has garnered significant commercial attention. Polypyrrole is a black, powdery substance that was initially created by chemically oxidising a pyrrole monomer in the presence of hydrogen peroxide. When doped with halogenic electron acceptors like bromine or iodine, polypyrrole exhibits a constant conductivity of 10^5 Sm^{-1} and acts like an insulating material in its undoped virgin state (Kiebooms et al., 2001). Although bulk polypyrrole has 15% crystallinity and is amorphous in nature, the crystalline region is in the monoclinic phase (Vernitskaya and Efimov, 1997).

According to Moss and Burford (1992) and Kang et al. (1991), thermal degradation can happen as a result of the loss of dopant anions. For electrochemically synthesised polypyrrole, which has a thickness of 1 mm and a yellow-blackish colour, transformation happens by an increase in protonation concentration and has higher stability in air and high thermal stability in the range of 300 °C. To produce highly conductive polypyrrole, electrochemical synthesis is a popular synthesis process whose steps and procedures are comparable to those of other conducting polymers (Fig. 1). Owing to this technique's smaller anode, the product yield is restricted. The primary benefit of this technology over alternative approaches is its ability to regulate the electrochemical parameters, which in turn allows us to manage the thickness and morphology (Istakova et al., 2019; Ozkazanc and Zor, 2013; Koinkar et al., 2016; Tang et al 2019). There are several different mechanisms for electrochemical synthesis. Here, deprotonation causes the development of a free radical cation in this polymerization pathway, which then targets the neutral monomer unit.

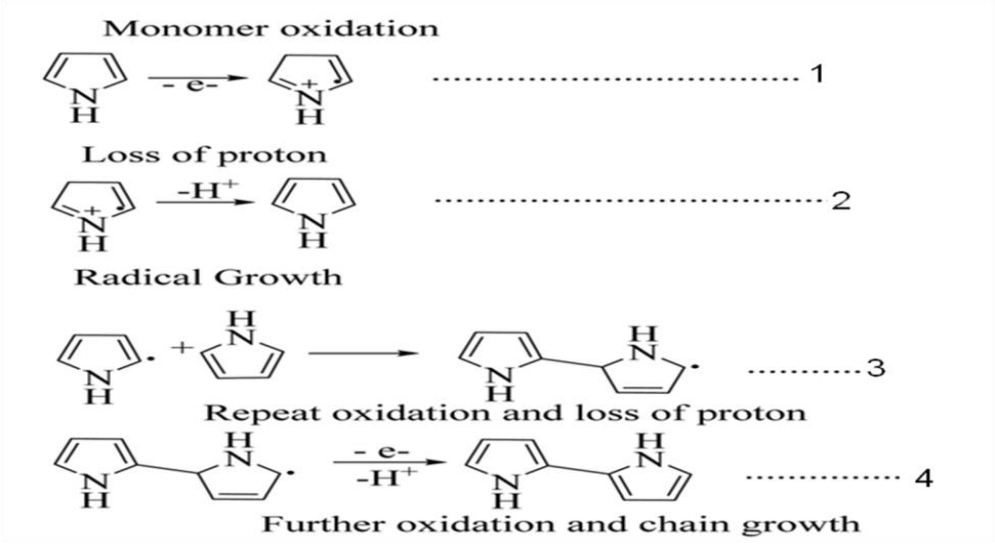

Fig. 1: Mechanism of electrochemical synthesis of polypyrrole.

The dimeric molecule may undergo further oxidation, leading to chain expansion, following the reoxidation of the dimeric radical and proton loss. Experimental research revealed that protons are released during the oxidation of pyrrole (Chandler and Pletcher, 1986). The first synthesis of polypyrrole used the oxidation of a pyrrole monomer in the presence of H_2O_2 to produce an amorphous, powdery, blackish substance (S. C. Rasmussen, 2015). In organic solvents, pyrrole black is insoluble, and its conductivity is restricted to the range of 10^{10} to 10^{11} s cm^{-1}. When doped with a halogen electron acceptor, it can be made with acid and peroxide, and its conductivity will rise. Chemical oxidants that are commonly utilised include aqueous or anhydrous $FeCl_3$, as well as various salts of iron (III) or copper (II) (Yussuf et al., 2017).

A few variables impact the yield and conductivity: (1) oxidant employed and solvent type; (2) pyrrole/oxidant ratio; (3) reaction time and temperature. When polypyrrole is prepared with an $FeCl_3$ oxidant, the final product is doped with Cl anions.

$$n C_4H_5N + (2 + y)n\ FeCl_3 / [(C_4H_3N)_n y + ny\ Cl^-]^+ + (2 + y)\ n FeCl_2 + 2n\ HCl$$

The synthesis of highly conductive polypyrrole involves adjusting an aqueous solution's oxidation potential through the addition of an oxidant. In addition to metallic salts, polypyrrole has been produced in a variety of solvents by employing a halogen electron acceptor, such as bromine or iodine (Kiebooms et al., 2001).

APPLICATION OF POLYPYRROLE

PPy's exceptional electrical, optical, and biological qualities make them suitable for use in energy storage, biomedicine, sensing, and other domains.

1. Energy Storage

The synthesis of PPy is essential to the fabrication of energy storage devices because PPy nanoparticles can be employed as the electrodes of energy storage devices (Peng et al., 2014). The production of PPy-based nanomaterials is comparatively advanced, and various techniques (such as radiolysis polymerization, electrospraying, greener mechanochemical routes, etc.) can be used to prepare nanomaterials with the necessary size and morphology to produce electrode materials with exceptional performance (Karim et al., 2010; Monfared et al., 2019).

2. Battery

The application of PPy nanoparticles to batteries has been concentrated on three areas: fuel cells (Xia et al., 2013; Wu et al., 2014), dye-sensitized solar cells (Jeon et al., 2011; Hwang et al., 2014), and lithium and sodium batteries (Ma et al., 2015).

3. Supercapacitor

In addition to their high specific electric capacity, PPy-based supercapacitors have drawn a lot of interest in the supercapacitor community. Researchers have worked tirelessly to improve the electrical performance and stability of PPy-based supercapacitors due to their low stability (Zhang et al., 2013; Wang et al., 2014). Using a modified gas phase polymerization, Santino et al. (2014) coated a high aspect ratio bristle-like nano-PPy continuous network on a graphitic hard carbon paper current collector. High discharge rates show good performance from electrodes based on nano-PPy. PPy nanoparticles have been reported for use in flexible supercapacitor applications, in addition to their traditional use as supercapacitors (Shi et al., 2014; Wei et al., 2017). A straightforward and adaptable synthesis method for employing PPy hydrogels with adjustable 3D microstructures as electrically active components for high-performance, flexible solid-state supercapacitors was published by Shi et al. in 2014. During extended cycling, the flexible symmetric PPy hydrogel-based supercapacitors demonstrated strong electrochemical stability and capacitive performance.

4. Drug Delivery and Release

The benefits of PPy-based polymers and nanomaterials include facile drug loading, minimal impact on drug activity, and a regulated rate of drug release. Using a straightforward microemulsion polymerization method, Samanta et al. (2015) created PPy NPs with a good drug loading capacity (15 wt%) and stable dispersion in solution. Drug release from the manufactured PPy NPs can be controlled by varying the pH, the drug's charge, and the addition of a little quantity of charged amphiphiles.

5. Photoacoustic and Photothermal Therapy

With its exceptional photostability, photothermal conversion capabilities, and strong biocompatibility, PPy nanoparticles have a wide range of potential applications in the photothermal therapy space. The most popular and original PPy nanomaterial for photothermal therapy is PPy NPs (Zhang et al., 2018; Theune et al., 2019).

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