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POLYMERIZATION TECHNIQUES OF CONDUCTING POLYMER POLYPYRROLE

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ABSTRACT:

This review concludes by addressing the challenges and future directions in the field, emphasizing the need for environmentally sustainable, efficient, and scalable methods to meet the growing demand for conducting polymers in advanced technological applications. Conducting polymers (CPs) have garnered great attraction due to their exceptional electrical, optical, and mechanical qualities, making them innovative materials for vast applications, including in sensors, energy storage devices, and flexible electronics. This review focuses on key polymerization techniques of Polypyrrole used to synthesize conducting polymers, such as chemical polymerization, electrochemical polymerization, and Electro spinning, Micro emulsion polymerization, Vapor-Phase polymerization, Mechano-chemical Polymerization. Additionally, advancements in enzymatic and vapor-phase polymerization techniques are also discussed, highlighting their potential for producing high- quality conducting polymers with enhanced properties. The review gives out a general outlook of synthesis and conductivity of Polypyrrole.

Keywords: Conducting Polymers (CP), Polypyrrole (PPy), Pyrrole (Py),

1. INTRODUCTION:

Synthesis of polymer Nano-composites is an important part of polymer Nano-technology. By adding the Nano-metric inorganic compounds, there is an improve in properties of polymers and therefore it has a lot of applications due to the inorganic material present in the polymer. PPy has quality that it has high electrical conductivity, stable at room temperature, and has redox property [1]

Conducting polymers(CPs) Nano-materials surface modification is good, biocompatibility, and large surface area, because of these qualities conducting polymer is best in use for electronic and Opto-electronic sensing system. Various conducting Nano materials are Polypyrrole (PPy), Polyaniline (PANI), PolyThiophene (PTh), Polythiophene (PT), Poly-acetylene (PA), Polyparaphenylene (PPP), Polyparavinylene (PPV), Poly-isothionaphtene (PITN), these conducting polymer can be effortlessly prepared by different methods of polymerization. **[2]**

The conjugated double-bonded backbone of conducting Polymer, come up with the electronic conductivity when doped with suitable dopants **[3].** Due to the alternating single and double bonds PPy is conducting in nature, due to this alternating single and double bond in the molecule there is delocalization of electron density **[4].** Conducting polymers are categorized as the cationic and anionic salts of highly conjugated polymers. The electron affinity has been altered through the use of doping which increases the degree of CPs charge carriers **[5].**

CPs have garnered significant academic and industrial interest due to their unique and inherent properties, such as semi conductivity, which can be modified through 'doping' processes related to oxidation or reduction **[6].** Some applications of Conducting Polymer Nano-composites are in conversion of energy and storage batteries, super capacitors & solar cells. In anti-static agents and elimination of heavy ions. In coating and corrosion mitigation. In sensors (chemical, biological & so on); catalysis. In bio-medical devices and tissues engineering. In electromagnetic interference shielding. On oxidation, Polypyrrole loses its conductivity and charge **[7].** Polypyrrole show electro-active behavior in organic electrolyte and aqueous solutions **[8].** Nano-tubes of PPy with diameters range 20nm to1µm is prepared by chemical process such as chemical synthesis, conductivity measurement and microscopy. Conductivity increased by successive synthesis of PPy inside pore result from increase of proportion of oriented PPy phase **[9].**

Moreover, significant advancements have been made in the synthesis of nanocrystals of metals, semiconductors, and magnetic materials through the colloidal chemical method. While the fabrication of metallic and inorganic semiconductor nanomaterials is well-established, the production of polymeric nanomaterials has remained relatively underexplored. CPs are organic materials that exhibit mechanical and physical properties related to conventional polymers and the unique electrical properties of metals. **[10]** In a PPy chain, monomer unit are bonded at α-α positions and pyrrole monomer is bonded at α-β and β-β positions. Conducting nature of PPy is due to the alternating single and double bonds, due to which delocalization of electron density occur in molecule as shown in fig 1. **[11]**

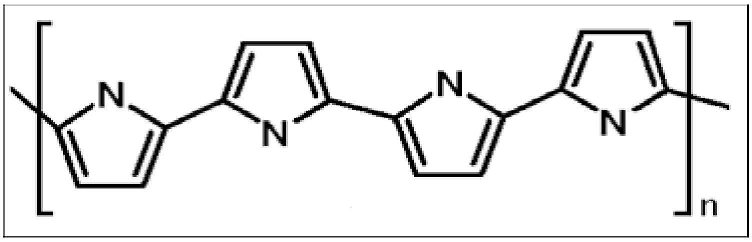

Figure 1: Polymeric structure of Polypyrrole

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1.1 CONDUCTING POLYMERS:

Different amount of PPy is combined with particles of colloidal ferric oxide, by which synthesis and characterization of a series of conducting Nano-composites is done. **[12].** Some CP's are Polyaniline (PANI), Polypyrrole (PPy), Poly (3,4 ethylenedioxythiophene) (PEDOT), Polythiophene (PT), Polyacetylene (PA), Polyparaphenylene (PPP), Polyparavinylene (PPV), Polyisothionaphthene (PITN) etc. which can be used for different purposes for example in super capacitors, water purifiers, electronic device, sensors, drugs release etc. Table-1 shows some conducting polymers (CP) and their conductivity and the doping type of that particular conducting polymer.

Table 1: Some Conducting Polymers with Their Conductivity Doping Types and Applications:

CONDUCTING POLY MERS	CONDUCTIVITY (SC M^{-1})	DOPING TYPE	APPLICATIONS
Polyaniline (PAN I)	30-200	n, p	conductive ink, conductive paint, and(ESD)
Polypyrrole (PPy)	10-700	N	Immunosensors, bioanalytical sensors, and supercapacitors
Poly(3,4ethylenedio xythiophene)(PEDO T)	0.4-400	N	Organic electronics ,Electrochemicals, Chemosensors
Polythio phene (PT)	10-1000	P	Electronic device, water purifier, and hydrogen storage
Polyacetylene (PA)	200-1000	n, p	Circuit,sensors, drug release,
Polyparaphenylene (PPP)	500	n, p	Medical, Semiconductors , Aerospace industries
Polyparavinylene (PPv)	1-1000	P	Light emitting diode , Photovoltaic devices
Polyisothionaphthene (PITN)	1-50	P	Optic display devices, Charge storage devices

1.2 POLYMERIZATION TECHNIQUES FOR NANOPARTICLES

Polymers can be synthesized by various types of polymerization techniques. The types of polymerization techniques are In-Situ polymerization and Ex-Situ Polymerization.

1.2.1 IN-SITU POLYMERIZATION:

In-situ polymerization actually means that "in place of" or "at original site" used for the preparation of Nano composites materials with dispersion and distribution of Nano particles. In-situ polymerization shows direct integration of well dispersed Nano particles in bulk polymer composite. Mixing of a Nano material in a simple, multiple or solution of monomer in presence of dispersed Nano material by polymerization. This polymerization is cost-effective, easy to automate and has the ability to integrate with many overheating and curing method. Below diagram shows the In-Situ method of polymerization process:

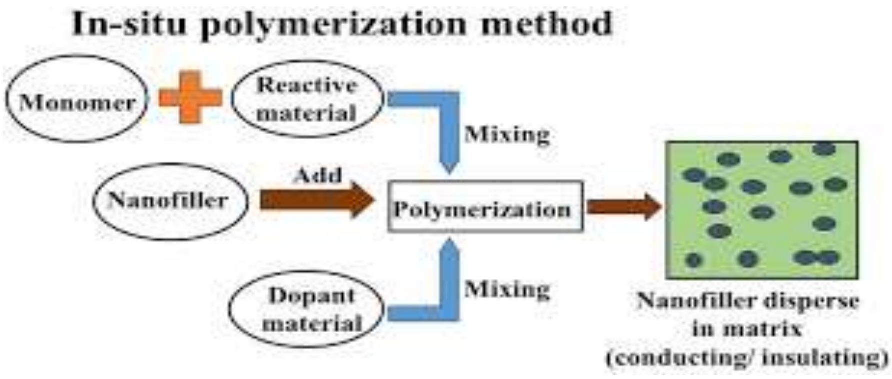

Figure. 2 In-situ Polymerization Process.

1.2.2 EX-SITU POLYMERIZATION:

Ex-situ polymerization is a method in which different precursors are generated separately and then mixed together to form a final product. In Ex-Situ Polymerization of PPy and oxidation of SiO2, NPs were carried out respectively. The application of Ex- Situ Polymerization Is in large scale industries.

Nano particles which have high dispersibility and stability against aggregation, is a challenge for Ex-Situ polymerization. **[13]**

PPy can be synthesized through oxidative Polymerization of the PPy monomer in the presence of Iron (III) Chloride ($FeCl_3$), Ammonium Persulfate (APS), or other oxidizing agents, using inorganic solvents (such as Acetonitrile and Propylene Carbonate) or aqueous media (water and acid solutions). **[14].**

1.3 METHODS OF SYNTHESIS OF POLYPRROLE:

Some of the common ways to synthesize Polypyrrole are: Chemical-oxidative Polymerization, Electro-spinning Polymerization, Electro-chemical Polymerization, Micro-emulsion Polymerization, Vapour-Phase Polymerization, Mechano-chemical Polymerization.

1.3.1CHEMICAL-OXIDATIVE POLYMERIZATION:

Polyprrole in fine powder form is produced through chemical oxidative polymerization. This method is highly cost-effective for large-scale production of PPy. The chemical oxidative polymerization of pyrrole is considered the most efficient approach to obtain PPy with high electrical conductivity in powder form, making it suitable for commercial applications. Spherical PPy nanoparticles have also been synthesized via chemical oxidative polymerization, using a surfactant or stabilizer in an aqueous solution **[15].** Below reactions shows polymerization of PPy by chemical oxidative polymerization. **[16].**

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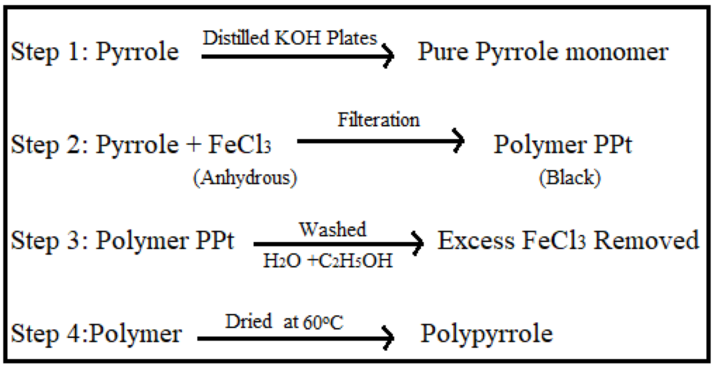

Figure 3: Systematic Representation of Chemical Oxidative Polymerization

2.1.1ELECTRO-SPINNING

Electro-spinning is a simple low cost method. It is a method which is used to fabricate continuous Nano scale fibers by using high voltage power supply with diameters ranging in between sub-micrometer to nanometers. Fabrication of PPy fiber can also be done using the melt electro-spinning and coaxial electro-spinning technique. **[17].** The prime drawback of this method is that the solution and melts used may form a connection between high voltage electrode, due to which electrode may get discharge which result in a flashover. **[18]** The following flow chart illustrates general method of Electro-spinning polymerization of PPy:

2.1.2ELECTRO-CHEMICAL POLYMERISATION:

Electrochemical polymerization is an irreversible process of polymer oxidation performed in any aqueous or no aqueous solvents. This method can produce layers of PPy film of desired thickness by controlling current Density, Electrode Potential and time of Electrodeposition. In this the Poly-Pyrrole chain is directly attached to electrode surface, the electrode coated by Polypyrrole can be used for energy storage applications, properties of Polypyrrole like conductivity and structure can be controlled during the preparation method. **[19].**

Initially, the pyrrole monomer undergoes oxidation to form a radical cation. Two such radical cations then couple to produce a Bi-Polymer, which, upon oxidation, forms Bi-pyrrole. Bi-Pyrrole is further oxidized to form Bi-Pyrrole radical cation and couple with Pyrrole monomer to form Tripyrrole. This continuous process of oxidation and deprotonation results into Polymeric chain of Polypyrrole. The major limitations of this polymerization technique is its inefficiency in producing PPy on a large scale. Additionally, it is both time-consuming and costly **[20].**

2.1.3MICRO-EMULSION POLYMERIZATION:

Micro-Emulsion Polymerization technique involve liquids which are immiscible like oil in water and have surfactant molecules. Surfactant with long carbon chain produce large number of nanoparticles, since they allow more internal space for polymerization. Advantages of using Micro-Emulsion polymerization is that it increases the yield of Polypyrrole nanoparticles and is also used to fabricate Polypyrrole. This method is preferred due to its low interfacial

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tension, highly thermodynamic stable and ability to dissolve immiscible liquids [**20**]. Hazarika and Kumar **[21]** has synthesized PPy nanoparticles by micro emulsion polymerization Py of with APS as oxidant and SDS as surfactant with various concentration of SDS. First the solution of SDS was prepared with 1 h stirring and then Py was to the solution with a continuous stirring of 2h. At last APS was added to the above solution and stirred constantly for another 24 h to complete the polymerization.

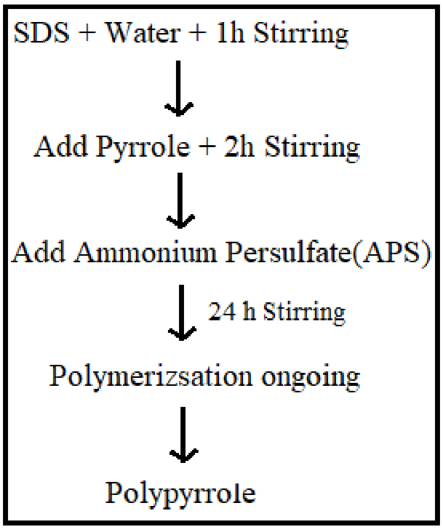

Figure 6: Flow Chart of Synthesis of Polypyrrole via Micro Emulsion Polymerization

Hazarika and Kumar **[21]** has synthesized PPy nanoparticles by mic ro emulsion polymerization Py of with APS as oxidant and SDS as surfactant with various concentration of SDS. First the solution of SDS was prepared with 1 h stirring and then Py was to the solution with a continuous stirring of 2h. At last APS was added to the above solution and stirred constantly for another 24 h to complete the polymerization.

2.1.4VAPOUR-PHASE POLYMERIZATION (VPP):

In this technique the monomer is introduced to the substrate (vapor form) coated with oxidant and the polymerization occurs at the vapors –oxidant interface [**22**]**.** VPP is effective, easy and inexpensive method of polymerization of a specific polymer on a particular substrate. [**23,24**]**.** This process is solvent-free as it takes place in vapor phase, [**22,25**]**.** Moreover, it is reported that CPs produced by this method show less conductivity compared to others that strict their usage in several electronic devices. [**22,26**]**.**

PPy films prepared by this method using $FeCl_3.6H_2O$ oxidant and poly (ethylene glycol-propylene glycolethyleneglycol) (PEG–PPG–PEG) solution as copolymer. These PPy films had shown high conductivity as compared to PPY. [**27**]

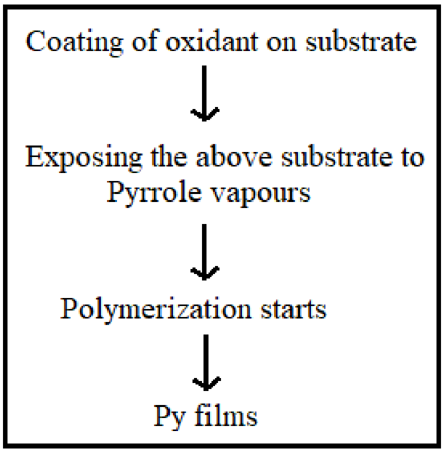

Figure 7: Flow Chart of Synthesis of Polypyrrole via Vapour-Phase Polymerization (VPP)

2.1.5MECHANO-CHEMICAL POLYMERIZATION:

When Mechanical energy produced by compression, shear, or friction etc. activates the chemical transformations, that is called Mechano-chemical methods. **[28]** Mechanochemical methods such as hand grinding and ball mining are considered to be efficient and cost effective. By these methods we can proceed with solvent free synthesis of conductive polymers**. [29]**

But this method is uncontrollable with respect to pressure, temperature, time and not suitable for handling liquids with low boiling point, moisture sensitive system and heterogeneous reactions. [**28].**

Palaniappan and Manisankar **[29]** has synthesized 80 nm spherical PPy nanostructures through a green mechanochemical. In this method a strong oxidant (KPS) is added to Pyrrole in 1:1 ratio and grinded manually for 20 minutes until the color of the reaction turns deep black. This black substance Pyrrole is then washed with water followed by Ethanol and dried in vacuum at 40C and used for further characterization.

However, mechanochemical polymerization poses challenges in controlling reactions involving moisture- and air-sensitive materials. Furthermore, the underlying mechanisms of mechanochemical polymerization remain poorly understood and warrant further investigation in this field**. [30]**

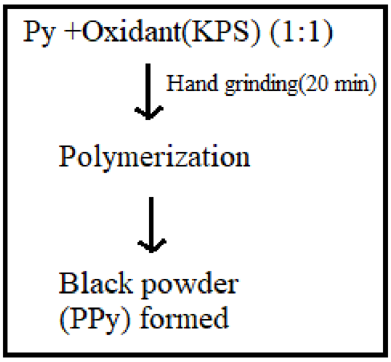

Figure.8 Flow Chart of Synthesis of Polypyrrole via Mechano-chemical Polymerization

3. CONCLUSION

From the above discussion it can be concluded that PPy is a conducting polymer which is utilized in wide-ranging applications (eg. Super Capacitors/ Electrodes, Nanocomposites, Gas Sensors, Biosensors, Drug Delivery, Protective Clothing, Anticorrosion Coatings, Actuators, and Adsorbents for the Removal of Heavy Metals and Dye. PPy is Electro active but on doping it changes into an ionic complex. Polymerization of Py can be done by different methods like Chemical Oxidative Polymerization, Electro-Spinning, Micro-Emulsion Polymerization, Electrochemical Polymerization, Vapor-Phase Polymerization, Mechano-Chemical Polymerization etc. through which PPy thin film or PPy powder can be obtained. The above discussion also includes the explanation of types of polymerization i.e. In-Situ type of polymerization and Ex-Situ type of Polymerization. The impact of these conducting polymers on environment is that they can be used for environmental remedies, waste water treatments, corrosion inhibitors and E- waste managements. Conducting polymers are less toxic and creates less damage to the environment.

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