



The chemistry of synthetic polymers and their applications

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Abstract

Without polymers, life would appear to be quite difficult. They constitute a very significant class of materials. They are present in everything we use daily, including rubber, plastic, glass, resins, paper, adhesives, and sticky tapes. Many components of living things, such as proteins, cellulose, and nucleic acids, are composed of polymers. Additionally, they are the building blocks of minerals including feldspar, quartz, and diamond. In this paper, we provide a literature survey on the polymerization process and its mechanisms, polymer structure, types of polymers, and conducting polymers. Polyaniline is unique among conducting polymers because of its low cost of monomers (aniline), observable electrical properties, good redox reversibility, high environmental stability, and ease of polymerization in the lab using chemical or electrochemical processes. The history of polyaniline development and its applications are briefly reviewed. Herein, Polyaniline was prepared *via* an oxidation synthesis using ammonium persulphate in an acid medium. The prepared polymer was confirmed by Fourier transform infrared spectroscopy (FTIR). In addition, we tested the conductivity of polyaniline by the formation electrical circuit using a small lamp.

Key Words:

Conducting polymers, Polyaniline, oxidation synthesis, ammonium persulphate, electrical circuit

1. Introduction A polymer is a material composed of many repeating subunits produced through the polymerization of several small molecules known as monomers (Painter and Coleman, 1997). Both synthetic and natural polymers have a wide range of uses in daily life, which makes them indispensable (McCrum et al., **1997**). Polymers vary from known synthetic plastics such as polystyrene to natural biopolymers such as DNA, and proteins that are vital to biological structure and purpose (Saberi et al., 2021). Although polymers can be synthesized in a variety of ways using polymerization techniques, the conformation of the monomer units, molecular weight, and size, monomer type and distribution, or polydispersity index all have a significant impact on the final properties of polymers, such as their mechanical, structural, and functional qualities. Polymers can be classified as either natural or synthetic depending on their origin, or and homopolymers heteropolymers depending on how they were synthesized (Alarie and Anderson, 1981).

In earlier research, scientists focused on the synthesis of conductive polymers, which are accomplished in the domains of energy, electronics, optics, and so on (Najjar et al., 2018; Du et al., 2017; Liao et al., 2016; Liao et al., 2018). Simple, lowcost techniques can be used to create conductive polymers (CPs) with a variety (Wang, 2022). of uses and Feng, Polyacetylene, polythiophene, polypyrrole, polyphenylene, and polyaniline (PANI) are the five primary categories of CPs [Nezakati et al., 2018]. The conjugated π system of the polymer backbone structure is the source of these

CPs' conductive characteristics (Nepomuceno et al., 2021).

Polyaniline is known as black aniline and has different forms depending on its oxidation level. Moreover, PANI is wellknown for its environmental stability, doping potential with protonic acids, and simplicity (Bhadra et al., 2020). PANI can be synthesized by connecting 1, 4coupling of aniline monomer parts (Park et al., 2016). While conductive polymers-PANI in particular-have several special benefits. they also have some disadvantages as well. For example, PANI's low processing capacity, rigidity, and lack of biodegradability limit its biological applications. The main problem with PANI is the poor solubility affected by the hard spine (Kenry and Liu, 2018).

Polyaniline is present in one of the three idealized oxidation states through the polymerization of aniline monomer: (a) leucoemeraldine (white/clear), (**b**) emeraldine (salt-green/base-blue), and (c) pernigraniline (blue/violet). Pernigraniline base is the term for fully oxidized PANI. PANI is totally reduced as the lecomeraldine base, while half of the oxidized PANI is reduced as the emeraldine base (Zhou et al., 2009). Among these, emeraldine is the most stable and conductive form. PANI's precise conductivity can be adjusted by

immersing the emeraldine base in an aqueous acidic solution of picric. phosphoric, or camphor sulfonic acid (Blinova et al., 2008). This depends on the synthesis technique used. PANI is obtained as a black powder and its emeraldine base form is difficult to treat due to its lack of solubility. The rigid polymer backbone and the hydrogen bonding contact between neighboring chains are the causes of the lack of solubility. Furthermore. PANI's emeraldine base form becomes unstable at a temperature used for melt processing.

PANI has potential applications in a of disciplines, including variety biomedical fields, organic electronics, and anti-corrosion materials as a result of its remarkable qualities, such as unique electrical features. chemical and environmental stability, easy preparation method, and low cost (Liao et al., 2019). As seen in Figure 1, it has a variety of uses, including chemical sensors (Sutar et al., 2007; Stamenov et al., 2012), corrosion devices (Schauer et al., 1998), solar cells (Bejbouji et al., 2010), and gas separation membranes (Illing et al., 2001). In this study, polyaniline was selected as an important conductive polymer to be synthesized via an oxidation process using ammonium persulphate in an acid medium. The prepared polymer will be confirmed by Fourier transform infrared spectroscopy (FTIR). Moreover, we will test the conductivity of polyaniline by the



formation electrical circuit using a light lamp.

Figure (1): Polyaniline in different applications.

- 2. The Theoretical Framework
- 2.1–Polymerization

The process of making polymers is called polymerization. After processing, these polymers are used to create a variety of plastic products. Smaller molecules known as monomers or building blocks are chemically joined to form larger molecules, or macromolecules, during the polymerization process. A polymer is made up of hundreds of these macromolecules (Sperling, 2005).

To obtain polymers with unique qualities appropriate for a range of uses, different polymerization processes are used. For instance, hundreds of ethylene monomers are polymerized to create polyethylene polymer, which is then utilized in a variety of applications requiring special qualities, such as carry bags, milk bottles, storage containers, trash barrels, rubbish liners, food packets, and corrugated conduits (Shrivastava, 2018).

2.2- Polymerization Mechanisms

Different polymerization reactions are categorized into several groups that are based on their reaction mechanism such as addition, condensation, ring opening, and other mechanisms as follows:

2.2.1. Addition or Chain Polymerization

The addition polymerization mechanism is the most widely among used ones. Furthermore, during polymerization, the monomer(s) and reactive site(s) on the polymer chain only react, causing the polymer chain to increase. Through a chain reaction, new monomer units are added one at a time. The polymerization process is carried out by repeated addition, whereby the reactive site is renewed at the conclusion of each growth phase upon the addition of a repeating unit to the expanding chain (Mita and Stepto, 1994). Simplifying the procedure would mean visualizing it as constructing a bicycle chain, with each link added one at a time to either or both ends. The chain lengthens as more links are added.

In addition, polymerization, unsaturated monomers-monomers with double or triple bonds-are typically employed. All monomers are used up in the addition polymerization process, and no byproducts are produced. Polyethylene, acrylics, polystyrene, polytetrafluoroethylene, polyoxymethylene (acetal), and polyvinyl chloride (PVC) are common examples of addition polymerization. Figure 2 shows a schematic representation of addition polymerization. It is evident that the repeating units on the left of the arrow are added to make the polymer on the right of the arrow symbol. R1 and R2 in this figure stand for functional groups or another type of atom group (McKeen, 2019; Ebewele, 2000)



Figure (2): Addition polymerization

2.2.1.1. Free Radical Polymerization

Free radical polymerization is the most basic kind of addition polymerization. A molecule having a free electron that is able to pair with an electron from another molecule is called a free radical. The three steps of polymerization could be described as follows using examples from polyethylene polymerization (Odian, 2004; Ghosh, 1990; Misra, 1993)

Chain Initiation

During this stage, a free radical (Ra^{*}) initiates the chain and produces a free radical building block. Unsaturated carbon-carbon monomers with a double or triple bond are usually involved in the start phase. The ethylene monomer's double bond opens to form a molecule with an unpaired electron or active center when an external initiator breaks down into a reactive group (free radicals Ra^{*}) to initiate the chain initiation phase (Ebewele, 2000). The ethylene monomer became the new radical when a free electron from the radical was transferred to the active center, shown by the (*). Here is an example of the initiation stage:

$Ra^* + CH_2 = CH_2 \rightarrow RaCH_2CH_2^*$ Chain Propagation

In this stage, ethylene monomer's free radical building block combines with other ethylene monomers to form a bigger free radical building block. The free radical building block forms bonds with nearby monomers along the length of the chain to stabilize the active centers (Ebewele, 2000). An active site is created for the subsequent attachment with each addition of a monomer unit. The following equations could be used to illustrate the propagation step:

 $RaCH_{2}CH_{2}^{*} + CH_{2} = CH_{2} \rightarrow RaCH_{2}CH_{2}CH_{2}CH_{2}^{*}$ $RaCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}^{*} + CH_{2} = CH_{2} \rightarrow RaCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}^{*}$

Chain Termination

During this stage, the chain's growth process comes to an end. The adding process won't stop until every monomer in the system is used up (the total chain length could be controlled by regulating the ethylene monomer supply). On the other hand, direct combination disproportionation or frequently puts an end to chain expansion. When free electrons from two developing chains combine to form a single chain, direct combination takes place, stopping the chain's expansion (Ebewele, 2000). Chain termination by direct combination could be described as

 $Ra(CH_2)_m^* + {}^*(CH_2)_n Ra \rightarrow Ra(CH_2)_m (CH_2)_n Ra$ 2.2.1.2. Ionic polymerization

chain Ionic polymerization is а polymerization in which the kinetic-chain carriers are ions or ion pairs (Penczek and Moad, 2008). Anionic polymerization and cationic polymerization are two further categories for it. Numerous common polymers, including butyl rubber. polyisobutylene, polyoxymethylene, polysiloxane, high density polyethylene, isotactic polypropylene, and others, are produced using ionic polymerization.

2.2.1.3. Coordination polymerization:

Coordination polymerization is a kind of chain polymerization in which a monomer molecule and a chain carrier are first coordinated in coordination polymerization (Penczek and Moad, 2008). Coordination polymerization is sometimes referred to as complexing polymerization or insertion polymerization. For chain growth, the activated monomer is introduced into the transition metal-carbon bond after the monomer has first been coordinated with the transition metal active center. Effective control the polymer's tacticity. over molecular weight, and PDI is possible with advanced coordination polymerizations. Furthermore. the chiral metallocene's racemic mixture may be divided into its enantiomers. Using an optically active catalyst, the oligomerization procedure yields an optically active branched olefin (Kaminsky, 1998).

2.2.2. Condensation or Step-growth polymerization:

Condensation polymerization is the second most frequent method for polymerization. In

this process, a tiny molecule (condensate), such as water or hydrochloric acid, is released as a consequence of the interaction between the repeating units and the expanding chain (Ghosh, 1990; Misra, 1993). Step-growth polymerization, as defined in polymer science, is a kind of polymerization process wherein bi- or multifunctional monomers react to generate dimers, trimers, longer oligomers, and ultimately long chain polymers (Ebewele, **2000**). Step-growth polymerization yields a wide range of synthetic and naturally occurring polymers, including polyesters, polyamides, polyurethanes, and many more. Because of the way the polymerization mechanism works, achieving a high molecular weight requires a significant level of reaction. Additionally, a monomer may have more than two reactive sites; in this case, the synthesis of branching polymers occurs. Figure 3 illustrates an example for Condensation polymerization.

 $\underset{HO-C-R_1-C-OH}{\overset{O}{\longrightarrow}} \overset{O}{\Longrightarrow} \overset{O}{\longleftarrow} \overset{O}{\longleftarrow} \underset{R_2-OH}{\overset{O}{\longrightarrow}} \overset{O}{\Longrightarrow} \overset{O}{\longleftarrow} \underset{R_1-C-O-R_2-O}{\overset{O}{\longleftarrow}} + \underset{H_2O}{\overset{O}{\longrightarrow}}$

Figure (3): Condensation polymerization with elimination of water

2.2.3. Ring-opening polymerization:

A polymerization known as "ring-opening polymerization" occurs when a cyclic monomer is polymerized into an acyclic or reduced-cycle monomeric unit. The ringopening polymerization often occurs under milder circumstances and produces less byproduct than the polycondensation process. It is simple to obtain a polymer with a high molecular weight. Polypropylene oxide, polytetrahydrofuran, polyepichlorohydrin, polyoxymethylene, polycaprolactam, and polysiloxane are examples of common ring-opening polymerization products (Shrivastava, 2018). 2.3-Polymer Structure

The ordering and configuration of polymer chains in space at the microscale is referred to as polymer morphology. The interactions between polymer chains determine a polymer's macroscopic physical characteristics. Polymeric materials can be linear, branched, or crosslinked depending on the intermolecular bonds that exist between the constituent chains.

2.3.1. Linear polymers

The repeating units of linear polymers are connected end to end to form a single, flexible chain. Physical forces work to keep the polymeric chains together. The chains are held together by the strong Vander Waals attraction of these polymers. Usually, monomers with a single end group are used to create linear polymers (Ebewele, 2000; Chanda. 2006). Polyethylene, PVC. polystyrene, and polyamides are a few typical examples of linear polymers. In general, linear polymers are rigid.

2.3.2. Branched Polymers

Side chains or branches that extend from the main chain characterize branched polymers. The repeating units that make up the main polymer chains also comprise the side chains, or branches. Side reactions that occur during polymerization give rise to the branches. Branching is likely to be supported by monomers that have two or more end groups. A polymer must have at least one full monomer unit in each of its side chains or branches in order to be classified as branched. Low-density polyethylene (LDPE) is one of the most popular examples; it is used in coatings for packaging materials as well as plastic bags, containers, textiles, and electrical insulation.

Because of the branched chains' decreased packing efficiency, branched polymers have a lower density. Polymers classified as long- or short-branched are distinguished by the length of their side chains or branches. Structures on long branches might be starshaped, asymmetrical, or comb-like. Despite the possibility of further branching, the branches do not join with another polymer chain (Chanda, 2006; Young and Lovell, 2011). 2.3.3. Crosslinked Polymers

As the name implies, crosslinked polymers are made up of neighboring polymer chains that are joined together in a three-dimensional network structure. Another name for the connections is crosslinks. The covalent connection between the chains or branches may result in crosslinks. In nature, crosslinks are often permanent. The polymer turns thermoset as soon as the crosslinks between the chains strengthen. The number of connection sites per unit volume, or crosslink density or degree of crosslink, is what distinguishes these polymers (Ebewele, 2000). Epoxies, bulk molding compounds, rubber, and other adhesives are typical examples. Figure 4 represents the chain configurations of linear, branched, and crosslinked polymers.



Figure (4): Schematic representation of linear, branched, and crosslinked polymers.

2.4-Types of polymers

Polymeric materials and substances may generally be categorized based on their structure or chemistry. Chemical formula, degree of substitution, tactility, weightaverage molecular weight $(\mathbf{M}\mathbf{w}),$ polydispersity, number-average molecular weight (Mn), and reactive functional groups are a few examples of structural descriptors (ECETOC, 2020). Polyolefine, Polyester, Polyether, Polyurethane, and so on are examples of main kinds of polymers. But even a single type of material, like polyethylene (PE), might have several subgroups, including high-density PE (HDPE) and low-density PE (LDPE), each having notably distinct characteristics (Andrady, 2017). Physicochemical parameters (such as water solubility, viscosity, melt-flow index, glass transition temperature, density, etc.) or morphological descriptors (such as physical state, form, degree of crystallinity, particle size, etc.) can also be used to classify the polymers. All structural and morphological characteristics as well as the physico-chemical properties of polymers are determined by the nature of a polymer product that consists of several components (ECETOC, 2020). Lastly, polymers can be broadly classified as fossilbased and bio-based, that is, polymers that

have been manufactured using bioresources. **Bioplastics** can be either biobased. biodegradable, or both (European Bioplastics, 2018). Natural polymers, also known as biopolymers, are another category of polymers that are found in nature. These natural polymers belong to the class of bioplastics biodegradable since it is anticipated that they would biodegrade in the environment.

2.4.1. Natural Polymers

biopolymers Natural polymers or are classified into polysaccharides, polypeptides (proteins), and nucleic acid polymers (polynucleotides) (Liu et al., 2018). Natural polymers as components of living systems are derived from plants, animals, and microorganisms (Liu et al., 2018). Advantages of natural polymers over synthetic polymers include biocompatibility, non-toxicity, biodegradability, and intrinsic antiviral properties (Rakowska et al., 2021).

2.4.2. Modified biopolymers

Often, natural polymers are altered to increase their stability for (industrial) applications. A variety of natural resources, including rice straw and agricultural by-products like cotton linters, flax fibers, maize, and cassava, are used to make these kinds of bioplastics (Polman et al., 2020). The structure is similar to the biopolymers that form their foundation. Thermoplastic starch (TPS), cellulose acetate (CA), and lignin-based polymers are examples of frequently used modified biopolymers (Polman et al., 2020).

2.4.3. Synthetic Polymers

In factories, synthetic polymers are purposefully created that way in order to benefit from certain qualities while in use. They could be bio-based or fossil-based. Due to their similar chemical characteristics, the same synthetic polymer produced from petroleum or natural sources should have the same biodegradability. Synthetic polymers offer a large variety of possible structures. having carbohydrates, Polymers such polyolefines (PE, PP), or polystyrol (PS), as well as those containing heteroatoms, like polyvinyl chloride (PVC), polyesters, like polyethyleneterephthalate (PET), polyether, polyamides, like Nylon 6, etc., might be among them.

The densities of plastic materials vary widely from 0.01 to 2.3 g/cm³ (Duis and Coors, 2016). However, it's important to remember that additives and environmental activities like weathering and fouling can change an item's density. Certain polymers, like polyethylene glycols [PEG], poly(vinyl alcohol) [PVA] or poly(vinyl pyrrolidone) **[PVP]**, anionic homo- and copolymers of acrylic acid, and cationic polyquaterniums [PQs], are soluble in water even though the majority of polymers, like plastics, are not (Bernhard et al., 2008; Duis et al., 2021; Eubeler, 2010).

Conductive polymers (CPs) are organic materials with unique electrical and optical properties. They can be made using simple, affordable methods and assembled into structures with multiple functions. The five main types of CPs are polyacetylene, polythiophene, polypyrrole, polyphenylene, and polyaniline (PANI) (Nezakati et al., 2018). The conductive properties of these CPs derive from the conjugated π system of the polymer backbone structure (Nepomuceno et al., 2021). We chose to study polyaniline because it has many features that attracted our attention due to its unique properties such as of low cost monomers (aniline), distinguishable electrical properties, excellent redox reversibility, high environmental stability and can be easily polymerized in labs either by chemical or electrochemical methods.

2.5-Polyaniline

One of the earliest conducting polymers that is known to exist is polyaniline, which has been thoroughly examined (MacDiarmid and Epstein, 1989; Syed and Dinesan, 1991; Geniès et al., 1990; Huang et al., 1986; Bhadra et al., 2009). It has been the most researched conducting polymer, followed by poly pyrrole (Stejskal al., 2010). et When polyaniline was first found in the 19th century, it was referred to as "aniline black" [Syed and Dinesan, 1991; Geniès et al., 1990). Upon discovering that it had electrical conductivity, several investigators started scrutinizing the characteristics of this substance.

2.5.1. History of Polyaniline Development

Instead of using a conductive polymer, polystyrene was doped, according to a 1977 study by Shirakawa (Shirakawa et al., 1977). It was discovered that under typical production conditions, only conductive polymers were sufficiently stable. When compared to other conductive polymers including polythene, polypyrrole, polyphenylene, polyphenylene vinylene, and polystyrene, PANI stands out as a strong contender due to a number of distinct characteristics. Because PANI has a high degree of heat resistance, it may be made with ease using chemical and electrochemical processes in a variety of organic solvents and even aqueous environments (Wang et al., 2017).

Furthermore, PANI's low cost, strong environmental stability, superior optical and electrical qualities, and strong anti-corrosion characteristics have all contributed to its growing popularity in commercial and industrial applications (Liao et al., 2017). Secondary batteries (Ma and Kan, 2013), solar cells (Gizzie et al., 2014), corrosion devices (Ramezanzadeh et al., 2018), organic lightemitting diodes (Xu et al., 2016), biological or chemical sensors (Pérez–Mitta et al., 2017), and electrorheological materials (Tang et al., 2018) are a few of these uses.

2.5.2. Electrical Properties of Polyaniline:

PANI, in its emeraldine salt form, has strong electrical conductivity, making it an appealing conductive polymer that finds widespread usage in the electrical industry. The basic emeraldine of PANI functions to protonate the nitrogen of the imine group when an acid is introduced, transforming it into a salt and changing the polymer's nonconductive state into an electrically conductive one (Babel and Hiran, 2021). Mostly, the range of PANI conductivity is from $\sigma < 10-10$ S/cm for undoped base emeraldine to σ 10 S/cm for doped salt

emeraldine (Huang et al., 1986; Mezan et al., 2020]. The doping of the polymer is linked to the process of enhancing the electrical conductivity or multiplying the variety of characteristics of PANI concurrently. Many researchers worldwide have been doping PANI with diverse types of chemical compounds for usage in a variety of applications in recent decades. This is done in an effort to increase the new compounds' (polymer compounds') electrical conductivity for usage in that application (Babel et al., 2021; Khalid et al., 2020).

2.5.3. Semiconducting Properties of polyaniline:

Because of its excellent electron conductivity, PANI is regarded as one of the most promising materials in the electronics industry. Yakuphanoglu and Senkal created the PANI diode, and the results of the electrical and thermal conductivity of the ionic liquid of PANI indicated that this polymer semiconductor is а p-type (Yakuphanoglu Senkal, 2007). and Conversely, PANI films doped with boric acid were made and their electrical characteristics were investigated. PANI films doped with boric acid were found to have semiconductive qualities; at room temperature, its electrical conductivity was measured at 1.02 × 104 S/cm. The PANI films doped with boric acid have an optical band gap of 3.71 eV. PANI is frequently utilized in organic field transistors and solar batteries due to its semiconducting characteristics (Yakuphanoglu and Senkal, 2008).

3. Methods of Research and the tools used

Chemicals:

Aniline (Adwic) as a monomer, Ammonium persulphate (Sigma–Aldrich) as an oxidizing agent, Hydrochloric acid, Fuming 37% (Adwic) as a doping agent, Acetone (Adwic) as a washing agent, Dimethylformamide (Adwic) as a solvent for conductivity analysis. All chemicals were used as received except aniline which was double distilled.

Preparation of Polyaniline (PANI):

Polyaniline was synthesized by chemical polymerization using aniline monomer, and ammonium persulphate $[(NH_4)_2S_2O_8]$ which is used as oxidant in presence of hydrochloric acid as follows:

10 g of the ammonium persulphate was dissolved in 100 ml (1 M/L) HCl and was cooled in an ice bath. Distilled aniline (4 ml) was dissolved in 100 ml of 1 M/L HCl and was also cooled to 0°C. The solution containing ammonium persulphate was slowly added dropwise into the aniline solution for a period of 45 minutes under constant stirring. The mixture was continuously stirred for another 1 h while cooling. After that, the mixture was kept in a room temperature for 24 h until fully polymerized. A green precipitate was formed, filtered off, and washed with 1 M HCl solution, followed by distilled water, and acetone was added. The obtained solid was dried in an oven for 6 h (Zaghloul et al., 2021;

FAYED et al., 1999). A diagram of the PANI synthesis method is disclosed in Figure 5. Characterization of PANI Powder:

FTIR Analysis of PANI:

After drying in an oven for 6 h at 50 \circ C to remove any remaining solvent, the PANI residue was exposed to FTIR to verify the functional groups present. Nicolet IS10 spectrophotometer (cm⁻¹) was used to confirm the existence of the key features of the substance. The spectral range was from 500 to 4000 cm⁻¹ using KBr disks at the faculty of education, chemistry department, Ain Shams University.

Conductivity of PANI:

The conductivity of the PANI powder was measured using the formation electrical circuit which consists of a power supply device, wire, a small lamp, and a solution of 0.1 g PANI in 25 ml DMF. When the connections are made, the circuit will "close" and current will flow through the circuit and light the lamp. The voltage used was 2.08 V.



Figure (5): The PANI synthesis method

4. Results of Research



Scheme 1: Polyaniline polymerization reaction



Figure (6): FT-IR of polyaniline powder



Figure (7): Electrical circuit of PANI



Figure (8): Molecular structures of three forms of polyaniline.

5. Interpretation of Results

Synthesis and characterization of Polyaniline (PANI):

According to numerous literature studies (Nezakati et al., 2018; Saeb et al., 2019; Zarrintaj et al., 2019; Banjar et al., 2023), PANI was synthesized by chemical oxidative polymerization using Aniline as the monomer, Ammonium persulfate (APS) as the oxidizing agent, and HCl solution to create high acidity media (Scheme 1).

The FT-IR spectrum of polyaniline, figure 6, revealed the stretching vibration of N-H at 3263 cm⁻¹. The two absorption bands at 1580 and 1483 cm⁻¹ attributed to C=C and C=N stretching modes for benzenoid and quinoid rings, respectively. Furthermore, the C-N stretching vibrations of the quinoid imine units' peak appeared at 1292 cm⁻¹. Finally, the vibration band at 875 cm⁻¹ is assigned to 1-4 substitution on the benzene ring (Liang et al., 2014; Chen et al., 2018; Sawant et al., 2021; Kowalczuk and Pitucha, 2019). The FT-IR study exhibits that polymerization of the aniline occurred and led to the formation of the polyaniline.

Application of polyaniline:

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Formation and characterization of electrical circuit with conductive polymer (PANI):

PANI is one of the most interesting conductive that show polymers high stability, environmental stable electrical conductivity, conductivity variations upon redox, and simplicity of synthesis (Macdiarmid et al., 1987; Sergeyeva et al., 1996). It is a highly promising material for a variety of nanoscale applications, especially biological and chemical sensors (Gerard et al., 2002; Dhand et al., 2011; Lange et al., 2008).

We investigate the conductivity of polyaniline by the formation electrical circuit which consists of a power supply device, wire, a small lamp, and solution of PANI in DMF. When we have a closed circuit, and all wires are connected, the small lamp is turned on as shown in Figure 7.

The mechanism of electrical conductivity of polyaniline is based on the delocalized positively charged free radicals, Conductivity is produced by these charge carriers moving along polymer chains. It is believed that when the quantity of radical cations in the polymer chains is maximized, maximal conductivity will be displayed. Thus, the protonation of the polymer, known as doping, is the mechanism of conductivity of polyaniline.

Polyaniline can be doped in two ways: *via* a non-redox process through acid treatment, and the other called a redox process in which leucoemeraldine can be converted to

emeraldine. It is the protonation reaction that causes a significant increase in the polymer conductivity observed by the p-doping process (oxidation). As a result of this pdoping, the aromatic structure changes into a quinoid form, and a positive charge is formed locally in the polymer chain. The increase in the oxidizing agent causes an increase in the quinone or imine form, boosting the protonation process, and higher conductivity due to the delocalized pi-electrons in the structure. These charge carriers are responsible for the electronic conduction in polyaniline (Focke and Wnek, 1988; FAYED et al., 2019). Figure 8 shows the molecular structures of three forms of polyaniline.

6. Conclusion

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In this research, we made a comprehensive overview of polymers that are produced through the polymerization of several small molecules known as monomers, and types of polymers like natural, synthetic, and modified polymers. Each polymer has a different backbone structure such as linear, branched, and crosslinked polymers. Some of them conduct electricity and some don't. We chose a very important conducting polymer such as polyaniline, highlighting the history of polyaniline development and its applications. PANI was synthesized by oxidative polymerization of aniline using ammonium persulfate as the oxidizing agent in the presence of HCl. The prepared polymer was confirmed by Fourier transform infrared spectroscopy (FTIR).

The conductivity of PANI was investigated by the formation electrical circuit which consists

of a power supply device, wire, a small lamp, and a solution of PANI in DMF. When we have a closed circuit, and all wires are connected, the small lamp is turned on, this proves the good conductivity of polyaniline. PANI is regarded as one of the most promising materials in the electronics industry.

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References and Sources

- Alarie, Y., & Anderson, R. C. (1981). Toxicologic classification of thermal decomposition products of synthetic and natural polymers. Toxicology and Applied Pharmacology, 57(2), 181–188.
- Andrady, A. L. (2017). The plastic in microplastics: A review. Marine pollution bulletin, 119(1), 12–22.

- Babel, V., & Hiran, B. L. (2021). A review on polyaniline composites: Synthesis, characterization, and applications. Polymer Composites, 42(7), 3142–3157.
- Banjar, M. F., Joynal Abedin, F. N., Fizal, A. N.
 S., Muhamad Sarih, N., Hossain, M. S.,
 Osman, H., ... & Zulkifli, M. (2023).
 Synthesis and Characterization of a Novel
 Nanosized Polyaniline. Polymers, 15(23),
 4565.
- Bejbouji, H., Vignau, L., Miane, J. L., Dang, M. T., Oualim, E. M., Harmouchi, M., & Mouhsen, A. (2010). Polyaniline as a hole injection layer on organic photovoltaic cells. Solar Energy Materials and Solar Cells, 94(2), 176–181.
- Bernhard, M., Eubeler, J. P., Zok, S., & Knepper, T. P. (2008). Aerobic biodegradation of polyethylene glycols of different molecular weights in wastewater and seawater. Water research, 42(19), 4791–4801.
- Bhadra, J., Alkareem, A., & Al-Thani, N. (2020).
 A review of advances in the preparation and application of polyaniline based thermoset blends and composites. *Journal of Polymer Research, 27*(5), 122.
- Bhadra, S., Khastgir, D., Singha, N. K., & Lee, J.
 H. (2009). Progress in preparation, processing and applications of polyaniline.
 Progress in polymer science, 34(8), 783–810.

- Blinova, N. V., Stejskal, J., Trchova, M., & Prokeš, J. (2008). Control of polyaniline conductivity and contact angles by partial protonation. Polymer International, 57(1), 66–69.
- Chanda, M. (2006). Introduction to polymer science and chemistry: a problem-solving approach. CRC press.
- Chen, J., Wang, H., Deng, J., Xu, C., & Wang, Y.
 (2018). Low-crystalline tungsten trioxide anode with superior electrochemical performance for flexible solid-state asymmetry supercapacitor. Journal of Materials Chemistry A, 6(19), 8986–8991.
- Cummings, I. (2020). Applicability of Analytical Tools, Test Methods and Models for Polymer Risk Assessment.
- Dhand, C., Das, M., Datta, M., & Malhotra, B. D. (2011). Recent advances in polyanilinebased biosensors. Biosensors and bioelectronics, 26(6), 2811–2821.
- Du, X., Zhang, Z., Liu, W., & Deng, Y. (2017). Nanocellulose-based conductive materials and their emerging applications in energy devices-A review. Nano Energy, 35, 299– 320.
- Duis, K., & Coors, A. (2016). Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care

products), fate and effects. Environmental Sciences Europe, 28(1), 2.

- Duis, K., Junker, T., & Coors, A. (2021). Environmental fate and effects of watersoluble synthetic organic polymers used in cosmetic products. Environmental Sciences Europe, 33(1), 21.
- Ebewele, R. O. (2000). Polymer science and technology. CRC press.
- Eubeler, J. P. (2010). Biodegradation of synthetic polymers in the aquatic environment (Doctoral dissertation, Universität Bremen).
- European Bioplastics. (2018). What are bioplastics? Material types, terminology, and labels-an introduction.
- FAYED, M., GOUDA, S. R., RADWAN, M., & BORHAM, Μ. (2019,January). AND **SYNTHESIS** CHARACTERIZATION OF ORGANIC POLYMER CONDUCTOR BASED ON POLYANILINE. In International Conference on Aerospace Sciences and Aviation Technology (Vol. 8, No. ASAT Conference, 4-6 May 1999, pp. 1-9). The Military Technical College.
- Focke, W. W., & Wnek, G. E. (1988). Conduction mechanisms in polyaniline (emeraldine salt). Journal of electroanalytical chemistry

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and interfacial electrochemistry, 256(2), 343–352.

- Genies, E. M., Boyle, A., Lapkowski, M., & Tsintavis, C. (1990). Polyaniline: A historical survey. Synthetic metals, 36(2), 139-182.
- Gerard, M., Chaubey, A., & Malhotra, B. D. (2002). Application of conducting polymers to biosensors. Biosensors and bioelectronics, 17(5), 345–359.
- Ghosh, P. (1990). Polymer science and technology. Tata McGraw-Hill Education.
- Gizzie, E. A., Niezgoda, J. S., Robinson, M. T., Harris, A. G., Jennings, G. K., Rosenthal,
 S. J., & Cliffel, D. E. (2015). Photosystem I-polyaniline/TiO 2 solid-state solar cells: simple devices for biohybrid solar energy conversion. Energy & Environmental Science, 8(12), 3572–3576.
- Huang, W. S., Humphrey, B. D., & MacDiarmid,
 A. G. (1986). Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 82(8), 2385–2400.
- Illing, G., Hellgardt, K., Wakeman, R. J., & Jungbauer, A. (2001). Preparation and characterisation of polyaniline-based

membranes for gas separation. Journal of Membrane Science, 184(1), 69–78.

- Kaminsky, W. (1998). Highly active metallocene catalysts for olefin polymerization. Journal of the Chemical Society, Dalton Transactions, (9), 1413–1418.
- Kenry, & Liu, B. (2018). Recent advances in biodegradable conducting polymers and their biomedical applications. Biomacromolecules, 19(6), 1783–1803.
- Khalid, N., Abd Razak, J., Hasib, H., Ismail, M., Mohamad, N., Junid, R., & Puspitasari, P. (2020, October). A short review on polyaniline (PANI) based nanocomposites for various applications: enhancing the electrical conductivity. In IOP Conference Series: Materials Science and Engineering (Vol. 957, No. 1, p. 012028). IOP Publishing.
- Kowalczuk, D., & Pitucha, M. (2019). Application of FTIR method for the assessment of immobilization of active substances in the matrix of biomedical materials. Materials, 12(18), 2972.
- Lange, U., Roznyatovskaya, N. V., & Mirsky, V. M. (2008). Conducting polymers in chemical sensors and arrays (invited review).
- Liang, S., Yi, M., Shen, Z., Liu, L., Zhang, X., & Ma, S. (2014). One-step green synthesis of

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graphene nanomesh by fluid-based method. RSC Advances, 4(31), 16127-16131.

- Liao, G., Chen, J., Zeng, W., Yu, C., Yi, C., & Xu, Z. (2016). Facile preparation of uniform nanocomposite spheres with loading silver nanoparticles on polystyrenemethyl acrylic acid spheres for catalytic reduction of 4-nitrophenol. The Journal of Physical Chemistry C, 120(45), 25935– 25944.
- Liao, G., Gong, Y., Yi, C., & Xu, Z. (2017). Soluble, antibacterial, and anticorrosion studies of sulfonated polystyrene/polyaniline/silver nanocomposites prepared with the sulfonated polystyrene template. Chinese Journal of Chemistry, 35(7), 1157–1164.
- Liao, G., Li, Q., & Xu, Z. (2019). The chemical modification of polyaniline with enhanced properties: A review. Progress in Organic Coatings, 126, 35-43.
- Liao, G., Li, Q., Zhao, W., Pang, Q., Gao, H., & Xu, Z. (2018). In-situ construction of novel silver nanoparticle decorated polymeric spheres as highly active and stable catalysts for reduction of methylene blue dye. Applied Catalysis A: General, 549, 102–111.
- Liu, F., Chen, Q., Liu, C., Ao, Q., Tian, X., Fan, J., ... & Wang, X. (2018). Natural polymers

for organ 3D bioprinting. Polymers, 10(11), 1278.

- Ma, Z., & Kan, J. (2013). Study of cylindrical Zn/PANI secondary batteries with electrolytes containing alkylimidazolium ionic liquid. Synthetic metals, 174, 58–62.
- MacDiarmid, A. G., & Epstein, A. J. (1989). Polyanilines: a novel class of conducting polymers. Faraday Discussions of the Chemical Society, 88, 317–332.
- MacDiarmid, A. G., Chiang, J. C., Richter, A. F., & Epstein, A. A. (1987). Polyaniline: a new concept in conducting polymers. Synthetic Metals, 18(1–3), 285–290.
- Marins, J. A., Soares, B. G., Fraga, M., Müller, D., & Barra, G. M. (2014). Self-supported bacterial cellulose polyaniline conducting membrane as electromagnetic interference shielding material: effect of the oxidizing agent. Cellulose, 21, 1409–1418.
- McCrum, N. G., Buckley, C. P., & Bucknall, C.B. (1997). Principles of polymer engineering. Oxford University Press.
- McKeen, L. W. (2019). *The effect of UV light and weather on plastics and elastomers*. William Andrew.
- Mezan, S. O., Hello, K. M., Jabbar, A. H., Hamzah, M. Q., Tuama, A., Roslan, M. S., & Agam, M. A. (2020). A review on synthesis of conducting with polyaniline

20

rice husk ash silica nanocomposites and application. International Journal of Psychosocial Rehabilitation, 24(03).

- Misra, G. S. (1993). *Introductory polymer chemistry*. New Age International.
- Mita, I., Stepto, R. F. T., & Suter, U. W. (1994).
 Basic classification and definitions of polymerization reactions (IUPAC Recommendations 1994). Pure and Applied Chemistry, 66(12), 2483–2486.
- Najjar, R., Katourani, S. A., & Hosseini, M. G. (2018).Self-healing and corrosion performance of protection organic polysulfide@ urea-formaldehyde resin core-shell nanoparticles in epoxy/PANI/ZnO nanocomposite coatings on anodized aluminum alloy. Progress in Organic Coatings, 124, 110-121.
- Nepomuceno, N. C., Seixas, A. A. A., Medeiros,
 E. S., & Mélo, T. J. A. (2021). Evaluation of conductivity of nanostructured polyaniline/cellulose nanocrystals (PANI/CNC) obtained via in situ polymerization. Journal of Solid–State Chemistry, 302, 122372.
- Nezakati, T., Seifalian, A., Tan, A., & Seifalian, A. M. (2018). Conductive polymers: opportunities and challenges in biomedical applications. Chemical reviews, 118(14), 6766–6843.

- Odian, G. (2004). Principles of Polymerization John Wiley & Sons. Inc.: Hoboken, NJ.
- Painter, P. C., & Coleman, M. M. (1997). Fundamentals of polymer science: an introductory text. Technomic Pub. Co. P. 1. ISBN 978-1-56676-559-6.
- Park, C. S., Lee, C., & Kwon, O. S. (2016). Conducting polymer based nanobiosensors. Polymers, 8(7), 249.
- Penczek, S., & Moad, G. (2008). Glossary of terms related to kinetics, thermodynamics, and mechanisms of polymerization (IUPAC Recommendations 2008). *Pure and Applied Chemistry, 80*(10), 2163–2193.
- Pérez-Mitta, G., Albesa, A. G., Trautmann, C., Toimil-Molares, M. E., & Azzaroni, O. (2017). Bioinspired integrated nanosystems based on solid-state nanopores: "iontronic" transduction of biological, chemical and physical stimuli. *Chemical science*, 8(2), 890–913.
- Polman, E. M., Gruter, G. J. M., Parsons, J. R., & Tietema, A. (2021). Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: A review. Science of the Total Environment, 753, 141953.
- Rakowska, P. D., Tiddia, M., Faruqui, N., Bankier, C., Pei, Y., Pollard, A. J., ... & Gilmore, I. S. (2021). Antiviral surfaces and

coatings and their mechanisms of action. Communications Materials, 2(1), 53.

- Ramezanzadeh, B., Bahlakeh, G., & Ramezanzadeh, M. (2018). Polyanilinecerium oxide (PAni-CeO2) coated graphene oxide for enhancement of epoxy coating corrosion protection performance on mild steel. Corrosion Science, 137, 111– 126.
- Saberi, A., Bakhsheshi–Rad, H. R., Abazari, S., Ismail, A. F., Sharif, S., Ramakrishna, S.,
 ... & Berto, F. (2021). A comprehensive review on surface modifications of biodegradable magnesium-based implant alloy: Polymer coatings opportunities and challenges. Coatings, 11(7), 747.
- Saeb, M. R., Zarrintaj, P., Khandelwal, P., & Chauhan, N. P. S. (2019). Synthetic route of polyaniline (I): Conventional oxidative polymerization. In Fundamentals and Emerging Applications of Polyaniline (pp. 17–41). Elsevier.
- Sawant, S. A., Waikar, M. R., Rasal, A. S., Chodankar, G. R., Dhas, S. D., Moholkar, A. V., ... & Sonkawade, R. G. (2021). Chemical synthesis and supercapacitive evaluation of polyaniline nanofibers (PANINFs). Journal of Materials Science: Materials in Electronics, 32(9), 11865– 11876.

- Schauer, T., Joos, A., Dulog, L., & Eisenbach, C. D. (1998). Protection of iron against corrosion with polyaniline primers. Progress in Organic Coatings, 33(1), 20–27.
- Sergeyeva, T. A., Lavrik, N. V., Piletsky, S. A., Rachkov, A. E., & El'Skaya, A. V. (1996). Polyaniline label-based conductometric sensor for IgG detection. Sensors and Actuators B: Chemical, 34(1–3), 283–288.
- Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K., & Heeger, A. J. (1977).
 Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH) x. Journal of the Chemical Society, Chemical Communications, (16), 578–580.
- Shrivastava, A. (2018). Introduction to plastics engineering. William
- Sperling, L. H. (2005). Introduction to physical polymer science. John Wiley & Sons.
- Stamenov, P., Madathil, R., & Coey, J. M. D. (2012). Dynamic response of ammonia sensors constructed from polyaniline nanofibre films with varying morphology. Sensors and Actuators B: Chemical, 161(1), 989–999.
- Stejskal, J., Sapurina, I., & Trchová, M. (2010). Polyaniline nanostructures and the role of aniline oligomers in their formation.

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Progress in Polymer Science, 35(12), 1420– 1481.

- Sutar, D. S., Padma, N., Aswal, D. K., Deshpande,
 S. K., Gupta, S. K., & Yakhmi, J. V. (2007).
 Preparation of nanofibrous polyaniline films and their application as ammonia gas sensor.
 Sensors and Actuators B: Chemical, 128(1), 286–292.
- Syed, A. A., & Dinesan, M. K. (1991). Polyaniline—A novel polymeric material. Talanta, 38(8), 815–837.
- Tang, J., Wen, X., Liu, Z., Wang, J., & Zhang, P. (2018). Synthesis and electrorheological performances of 2D PANI/TiO2 nanosheets. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 552, 24–31.
- Wang, H., Wen, H., Hu, B., Fei, G., Shen, Y., Sun, L., & Yang, D. (2017). Facile approach to fabricate waterborne polyaniline nanocomposites with environmental benignity and high physical properties. Scientific reports, 7(1), 43694.
- Wang, Y., & Feng, W. (2022). Conductive Polymers and Their Composites. Springer Nature.
- Xu, R. P., Li, Y. Q., & Tang, J. X. (2016). Recent advances in flexible organic light-emitting diodes. Journal of Materials Chemistry C, 4(39), 9116–9142.

- Yakuphanoglu, F., & Şenkal, B. F. (2007). Electronic and thermoelectric properties of polyaniline organic semiconductor and electrical characterization of Al/PANI MIS diode. The Journal of Physical Chemistry C, 111(4), 1840–1846.
- Yakuphanoglu, F., & Şenkal, B. F. (2008). Electrical transport properties of an organic semiconductor on polyaniline doped by boric acid. Polymers for Advanced Technologies, 19(12), 1876–1881.
- Young, R. J., & Lovell, P. A. (2011). Introduction to polymers. CRC press.
- Zaghloul, M. Y. M., Zaghloul, M. M. Y., & Zaghloul, M. M. Y. (2021). Developments in polyester composite materials–An indepth review on natural fibres and nano fillers. *Composite Structures*, *278*, 114698.
- Zarrintaj, P., Vahabi, H., Saeb, M. R., & Mozafari,
 M. (2019). Application of polyaniline and
 its derivatives. In Fundamentals and
 Emerging Applications of Polyaniline (pp. 259–272). Elsevier.
- Zhou, D. D., Cui, X. T., Hines, A., & Greenberg, R. J. (2010). Conducting polymers in neural stimulation applications. *Implantable Neural Prostheses 2: Techniques and Engineering Approaches*, 217–252.

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