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SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS OF POLYMERS, BASED ON AROMATIC AMINES: A BRIEF REVIEW

Ramil RZAYEV*1,2,3, **Bakhtiyar A. MAMMADOV**3, **Fliur Z. MACAEV**1

1 *Laboratory of Organic Synthesis, Institute of Chemistry of the Moldova State University,*
str. Academiei 3, MD-2028, Chisinau, Republic of Moldova

2 *Department of Chemical Engineering, Baku Engineering University,*
Hasan Aliyev str. 120, Baku, Absheron, AZ0101, Azerbaijan Republic

3 *Institute of Polymer Materials, Azerbaijan National Academy of Sciences,*
Vurgun Str., 124, Sumgait, AZ5004, Azerbaijan Republic

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ABSTRACT

Aromatic amines represent one of the most extensively studied classes of organic compounds due to the valuable polymeric products they form and their exceptional properties. This review provides an overview of their synthesis, principal properties, a broad range of applications and some limitations.

Aniline and its derivatives are regarded as promising candidates for intrinsically conductive polymers (CPs), which can be employed as electroactive materials in electronics, energy storage, sensors, smart textiles, and biomedical technologies. Owing to their conjugated structures, tunable redox chemistry, and excellent environmental stability, aromatic-amine-based polymers-particularly polyaniline and its derivatives-remain among the most versatile materials in the field of synthetic metals. Their lightweight nature, chemical robustness, processability, and mechanical flexibility, combined with the ability to modulate electrical conductivity through protonic or oxidative doping, enable these materials to serve as potential alternatives to conventional metals, and semiconductors.

This review highlights recent advances in the synthesis, doping mechanisms, and structure–property relationships of aromatic-amine-based conductive aromatic polymers. Special attention is given to established synthetic routes, including chemical and electrochemical oxidative polymerization, interfacial and template-assisted methods, plasma and photochemical techniques, and emerging green synthesis strategies. This article aims to support the continued development of next-generation functional materials for advanced technological applications.

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* *Corresponding author:*
E-mail: ramilrzayev81@gmail.com

1. Introduction

Aromatic amines are a structurally important class of organic molecules in which an amine group is conjugated with an aromatic ring, imparting distinctive electronic and reactivity profiles. Since their discovery, conducting polymers (CPs) have attracted considerable attention due to their unique combination of electronic conductivity and polymeric properties, prompting numerous comprehensive reviews of their synthesis, structure, and applications. The pioneering work in this field was recognized with the 2000 Nobel Prize in Chemistry, awarded to MacDiarmid, Shirakawa, and Heeger for demonstrating that organic polymers can exhibit metallic conductivity under suitable conditions [1–6] This breakthrough sparked widespread interest in a variety of conducting polymers, including polythiophene, poly-pyrrole, and polyaniline. These materials are characterized by an extended π-conjugated system, in which a large number of π-electrons are delocalized across the polymer backbone [7, 8]. The delocalized π-electron system in conducting polymers underpins their intrinsic electrical conductivity, while the presence of a finite energy gap between the valence and conduction bands imparts semiconducting behavior, allowing charge transport under appropriate conditions [9, 10].

Among conducting polymers aniline and its derivatives have been particularly notable, as their oxidative polymerization produces materials with tunable redox states, good environmental stability, and versatile processability. Furthermore, aromatic diamines such as o-, m-, and p-phenylenediamines provide extra functionality, enabling the formation of ladder-type or phenazine-like structures with enhanced electronic and physicochemical properties, broadening their potential applications in sensing, energy storage, optoelectronics, and biomedical technologies [11].

This review provides a comprehensive overview of the development of aromatic conducting polymers derived from key monomers, including aniline, o-toluidine, and o-, m-, and p-phenylenediamines. It examines their classification (Figure 1), synthetic methodologies, structural and physicochemical characterization, and diverse potential applications. In addition, the review critically addresses the current limitations and challenges associated with these polymers, highlighting areas where further research is required to enhance their performance and broaden their practical applicability.

2. Classification of aromatic amines

Aromatic amines are a fundamental class of organic compounds characterized by the presence of one or more amino groups ($-NH_2$, $-NHR$, or $-NR_2$) directly attached to an aromatic ring. The simplest example is aniline ($C_6H_5NH_2$)[12–14]. Their unique structural features combine the nucleophilicity of the amino group with the stability and electronic properties of the aromatic system, making them highly versatile in chemical synthesis and industrial applications. These compounds serve as key intermediates in the production of dyes, pharmaceuticals, agrochemicals, and high-performance polymers. The classification of aromatic amines-based on the number of amino groups, substitution patterns, and type of aromatic ring-not only provides a systematic understanding of their structural diversity but also plays a critical role in predicting their chemical reactivity and suitability for specific applications. Given their broad utility, aromatic amines continue to be a focus of research in material science, medicinal chemistry, and polymer chemistry, particularly in the development of conductive polymers, functional materials, and biologically active molecules.

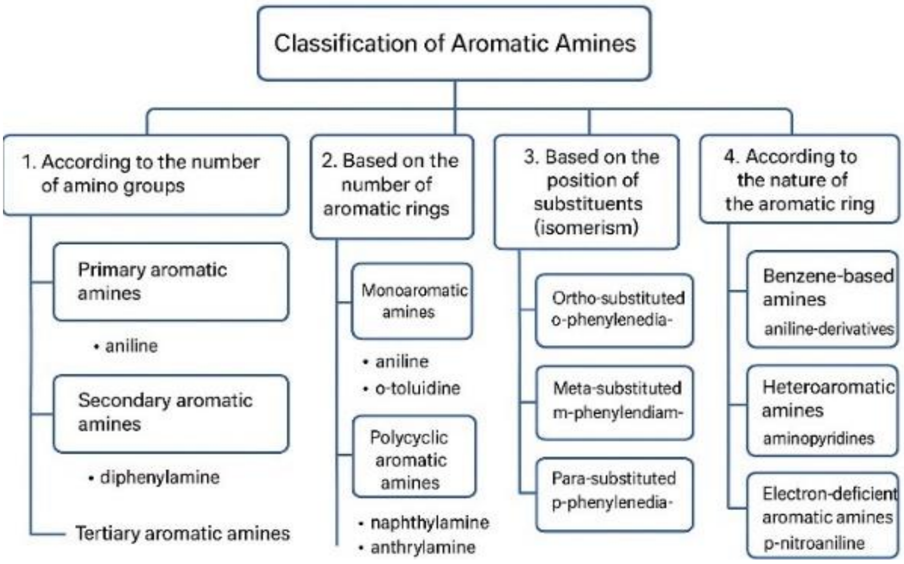

Figure 1. Classification of aromatic amines

2.1. Methods of polymer synthesis

Conductive polymers obtained from aromatic amines - such as aniline, toluidine isomers, and *o-/m-/p*-phenylenediamine - have attracted significant attention due to their unique redox activity, tunable conductivity, environmental stability, and broad applicability in electronics, sensors, catalysis, and energy storage systems. The method of synthesis plays a central role in defining the polymer's molecular structure, oxidation state, doping level, morphology, and resulting electronic properties. Accordingly, numerous synthetic approaches have been developed to manipulate polymer growth, control nanostructure formation, and tailor physicochemical characteristics to meet specific functional requirements. This section provides a comprehensive review of the principal synthesis routes employed for conductive polymers derived from aromatic amines, emphasizing mechanistic features, processing variables, structural outcomes, and application-relevant characteristics.

2.1.1. Chemical Oxidative Polymerization

Chemical oxidative polymerization (COP) remains the most extensively used method for synthesizing conductive polymers from aromatic amines. In this approach, polymerization is initiated by the oxidation of the monomer in the presence of strong oxidants such as ammonium or potassium persulfate, ferric chloride, or ceric ammonium nitrate. When dissolved in acidic media, aromatic amines become protonated, facilitating the generation of radical cations upon oxidation. These reactive intermediates undergo head–tail or para–para coupling to form dimers, oligomers, and ultimately high-molecular-weight polymer chains. For aniline and *phenylenediamine* derivatives, COP typically yields polymers in mixed oxidation states, including leucoemeraldine, emeraldine, and pernigraniline forms. The final oxidation state strongly influences conductivity and is largely dictated by oxidant concentration, reaction temperature, and acidity of the medium. The method is versatile, allowing production of powders, colloidal dispersions, nanofibers, nanotubes, and composite structures depending on the choice of surfactants, templates, co-monomers, and dopants. Its simplicity, scalability, and compatibility with various functional additives make COP the dominant route for industrial-scale production [15–17].

2.1.2 Electrochemical Polymerization

Electrochemical polymerization provides a highly controlled method to deposit conductive polymer films directly onto electrode surfaces. In this technique, the aromatic amine undergoes anodic oxidation under a precisely controlled potential or current. The resulting radical cations couple at the electrode interface, leading to the sequential formation of oligomers and polymer chains tightly adhering to the substrate. This method offers several key advantages: it eliminates the need for chemical oxidants, produces highly pure materials, and enables precise tuning of film thickness, morphology, redox state, and doping level. Electrochemical polymerization of aniline and various phenylenediamines often results in smooth, uniform, and strongly adherent films with excellent electroactivity. Cyclic voltammetry, chronoamperometry, and chronopotentiometry are typically employed to control polymer growth. This approach is widely used in the fabrication of electrochemical sensors, anticorrosive coatings, redox-active thin films, and energy-storage electrodes [18–22].

2.1.3. Enzymatic Polymerization

Enzymatic polymerization has emerged as an environmentally benign alternative to traditional oxidative methods. Enzymes such as laccase and horseradish peroxidase catalyze the oxidation of aromatic amines under mild aqueous conditions, generating radical species with high selectivity. This form of biocatalytic oxidation typically produces oligomers and polymers with fewer structural defects and narrower molecular-weight distributions compared to chemical oxidative routes.

In the case of aniline and phenylenediamines, enzymatic approaches often yield materials with enhanced biocompatibility and improved environmental sustainability. Because the reaction occurs without harsh oxidants or extreme acidity, the resulting polymers are suitable for biomedical applications, biosensing, and environmentally friendly coatings. Control over pH, hydrogen peroxide concentration, enzyme loading, and reaction temperature is essential for determining polymer architecture and oxidation state [23–28].

2.1.4 Photochemical Polymerization

Photochemical polymerization relies on the use of ultraviolet irradiation or photo-initiators to drive oxidative coupling of aromatic amines. Upon exposure to light, photosensitizers and electron-transfer agents generate radical species from the monomer, initiating polymer growth. This method enables spatial control over polymerization and is particularly valuable for producing micro-patterned or lithographically structured films.

For aniline and substituted amines, photopolymerization can be conducted in solution or directly on surfaces, yielding thin, uniform films with tunable properties. The ability to restrict polymerization to illuminated regions facilitates fabrication of microelectrodes, photonic structures, and patterned conductive coatings. The structural features and conductivity of the resulting polymers depend on light intensity, exposure time, wavelength, and the presence of photosensitizing additives.

2.1.5. Plasma Polymerization

Plasma polymerization involves subjecting volatile monomers to a plasma discharge within a low-pressure environment. The energetic species present in the plasma partially fragment and activate the aromatic amine molecules, allowing them to recombine on a surface to form highly crosslinked polymeric films. The resulting materials are typically ultra-thin, pinhole-free, and highly adherent. Although plasma polymerization often leads to partially disordered structures with limited conjugation, optimizing plasma power, pressure, and monomer flow can preserve aromatic functionality and allow useful levels of conductivity. Plasma-deposited films of aniline and phenylenediamines offer exceptional conformality and chemical robustness, making them attractive for protective coatings, biomedical interfaces, and electronic insulation layers [29].

2.1.6. Vapor-Phase Polymerization

Vapor-phase polymerization (VPP) has become an important method for fabricating high-quality conductive polymer films. The technique involves depositing an oxidant layer-commonly ferric chloride, iron (III) tosylate, or ammonium persulfate - onto a substrate, followed by exposure to monomer vapor. The monomer diffuses into the oxidant-rich layer, initiating polymerization at a controlled rate. VPP is especially effective for deriving thin, uniform films of polyaniline and its derivatives with high crystallinity and excellent electrical conductivity. The absence of bulk solution enables more ordered chain growth and minimizes aggregation and impurity incorporation. Process parameters such as oxidant loading, humidity, temperature, and additives profoundly influence polymer morphology, nanostructure, and film conductivity. VPP has become a key technique in flexible electronics, antistatic coatings, and transparent conductive layers.

2.1.7 Solid-State Polymerization

Solid-state polymerization represents a solvent-free approach in which aromatic amine crystals undergo polymerization under elevated temperature, pressure, or irradiation. The constrained mobility of monomers in the solid state can promote highly ordered polymer structures and unique packing arrangements. Although this method is less commonly applied to aniline and phenylenediamines, several studies have demonstrated its utility for producing crystalline oligomers, nanostructured materials, and hybrid frameworks. Solid-state methods are attractive from a sustainability standpoint, offering minimal solvent use and low environmental impact. They also enable the formation of materials that may be difficult to access through traditional solution-phase polymerization [30–33].

2.1.8. Template-Assisted Polymerization

Template-assisted synthesis is a powerful means of directing the growth of conductive polymers into well-defined nanostructures. Hard templates such as anodic alumina, silica, or polycarbonate membranes are widely used to produce nanowires, nanotubes, and nanorods. Soft templates-such as surfactant micelles, microemulsions, or liquid-crystalline phases-guide the formation of nanospheres, nanofibers, and other self-assembled morphologies. When aromatic amines undergo oxidative or electrochemical polymerization within these templates, the resulting nanostructures exhibit enhanced surface area, improved ion transport, and increased electrochemical performance. Template-assisted polymerization is particularly advantageous for fabricating nanostructured polyaniline and phenylenediamine derivatives for sensing, catalysis, and energy-storage applications [34–37].

2.1.9. Interfacial Polymerization

Interfacial polymerization exploits the boundary between two immiscible phases - typically an aqueous solution containing the aromatic amine and an organic phase containing an oxidant or co-reactant. Polymerization occurs exclusively at the interface, yielding thin films, membranes, shells, or hollow nanostructures. For aromatic amines, this approach provides exceptional control over film thickness and enables the fabrication of ultrathin polyaniline membranes with uniform morphology. The confined nature of the interfacial region produces materials with reduced structural disorder and improved electronic properties. These films find applications in separation technologies, coating materials, and controlled-release systems [38–42].

2.1.10 Hydrothermal and Solvothermal Polymerization

Hydrothermal and solvothermal methods involve conducting polymerization reactions in sealed autoclaves at elevated temperatures and pressures. Under these conditions, aromatic amines exhibit enhanced solubility, reactivity, and diffusivity, promoting the formation of crystalline or hierarchically organized polymer structures.

Hydrothermal polymerization of aniline and phenylenediamines often results in nanorods, nanosheets, hollow spheres, or flower-like architectures with high structural coherence. These materials are promising for applications in catalysis, electrochemical devices, and advanced functional composites. The solvent type, reaction temperature, pressure, and duration critically determine the resulting morphology and polymer chain structure [43].

2.1.11. Emulsion and Miniemulsion Polymerization

Emulsion and miniemulsion techniques utilize surfactant-stabilized droplets to disperse aromatic amines in an aqueous medium. Oxidative polymerization proceeds within individual micelles or droplets, yielding polymer nanoparticles with well-controlled sizes and narrow distributions. Miniemulsion systems, with smaller and more stable droplets, provide superior control over particle uniformity. Polyaniline and substituted amine nanoparticles produced through these techniques possess high dispersibility, making them suitable for inks, coatings, and composite formulations. The method is compatible with large-scale industrial processing and allows incorporation of dopants, stabilizers, or functional particles into the polymer matrix [44, 45].

2.1.12. Sol–Gel Assisted Polymerization

Sol–gel assisted polymerization integrates conductive polymers with inorganic networks such as silica or metal oxides. During the solgel process, polymerization of the aromatic amine occurs simultaneously with the formation of a growing inorganic matrix, resulting in hybrid materials that combine the conductivity of organic polymers with the structural stability of inorganic hosts. These organic-inorganic hybrids exhibit enhanced thermal stability, mechanical strength, and environmental resistance. Incorporation of aniline or phenylenediamine derivatives within sol–gel networks enables precise control over morphology, porosity, and interfacial interactions. Such materials are widely used in sensors, catalysis, corrosion protection, and multifunctional coatings [46, 47].

Conclusion

The synthesis method profoundly influences the structural, electronic, and functional properties of conductive polymers derived from aromatic amines. Chemical oxidative polymerization and electrochemical deposition remain the most widely used techniques due to their simplicity and versatility, while emerging methods such as enzymatic, photochemical, and vapor-phase polymerization offer new opportunities for achieving highly controlled architectures and environmentally sustainable processing. Template-based, hydrothermal, and sol-gel-assisted approaches further expand the morphological diversity of these materials, enabling precise manipulation of nanoscale features critical for advanced applications. Collectively, these methods form a robust toolbox for tailoring the properties of aromatic-amine-based conductive polymers for next-generation electronic, electrochemical, sensing, and catalytic systems.

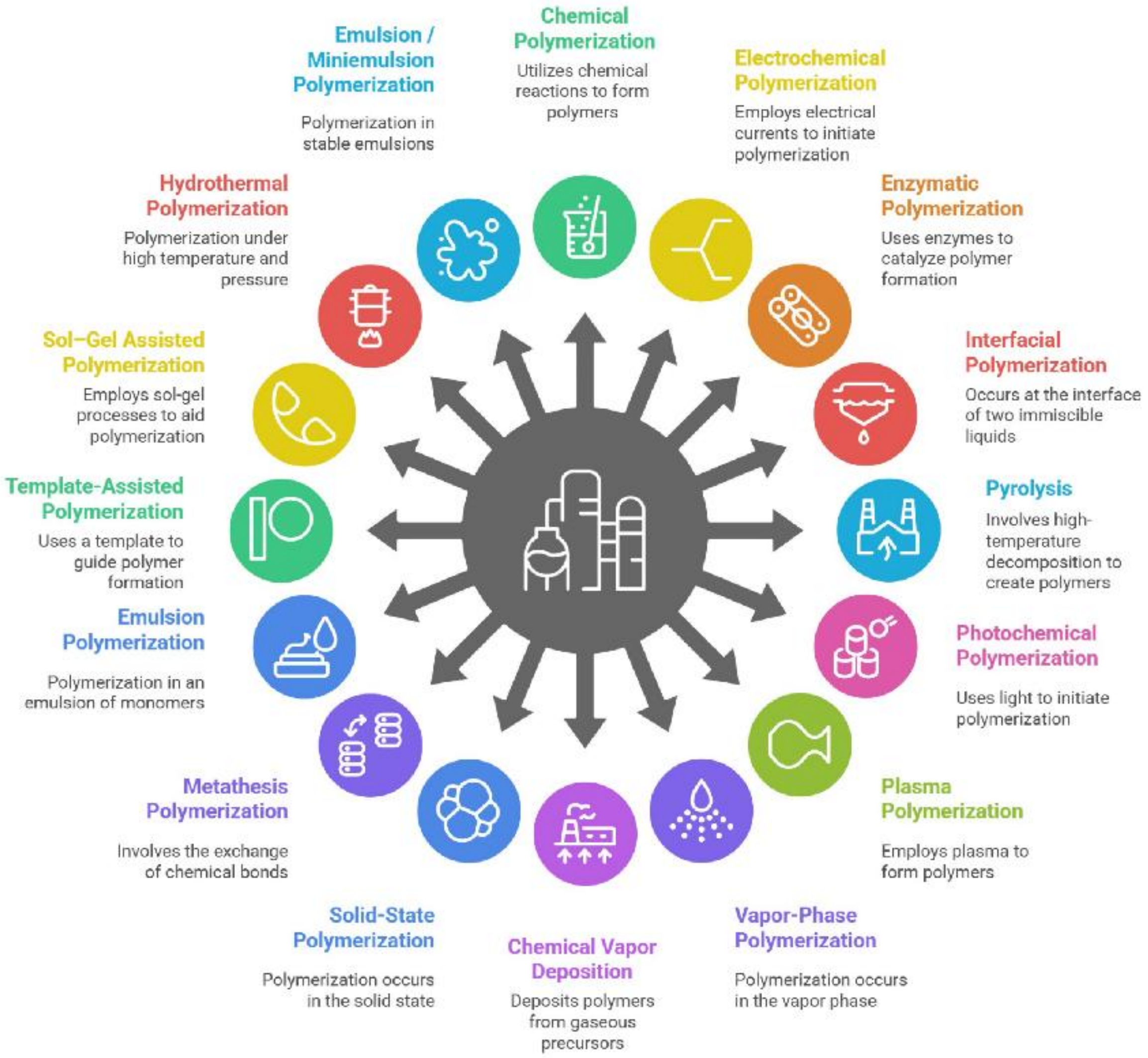

Figure 2. The synthesis methods of aromatic polymers

2.2 Characterization of Polymers

Polymer characterization is the process of determining the physical, chemical, thermal, mechanical, and structural properties of polymers. This is essential to understand their behavior, performance, and suitability for various applications, including conductive polymers, coatings, biomedical devices, and composites. Proper characterization ensures reproducibility, quality control, and guides further chemical modifications. In Figure 3, some essential characterization techniques of polymers are given [15, 48–51].

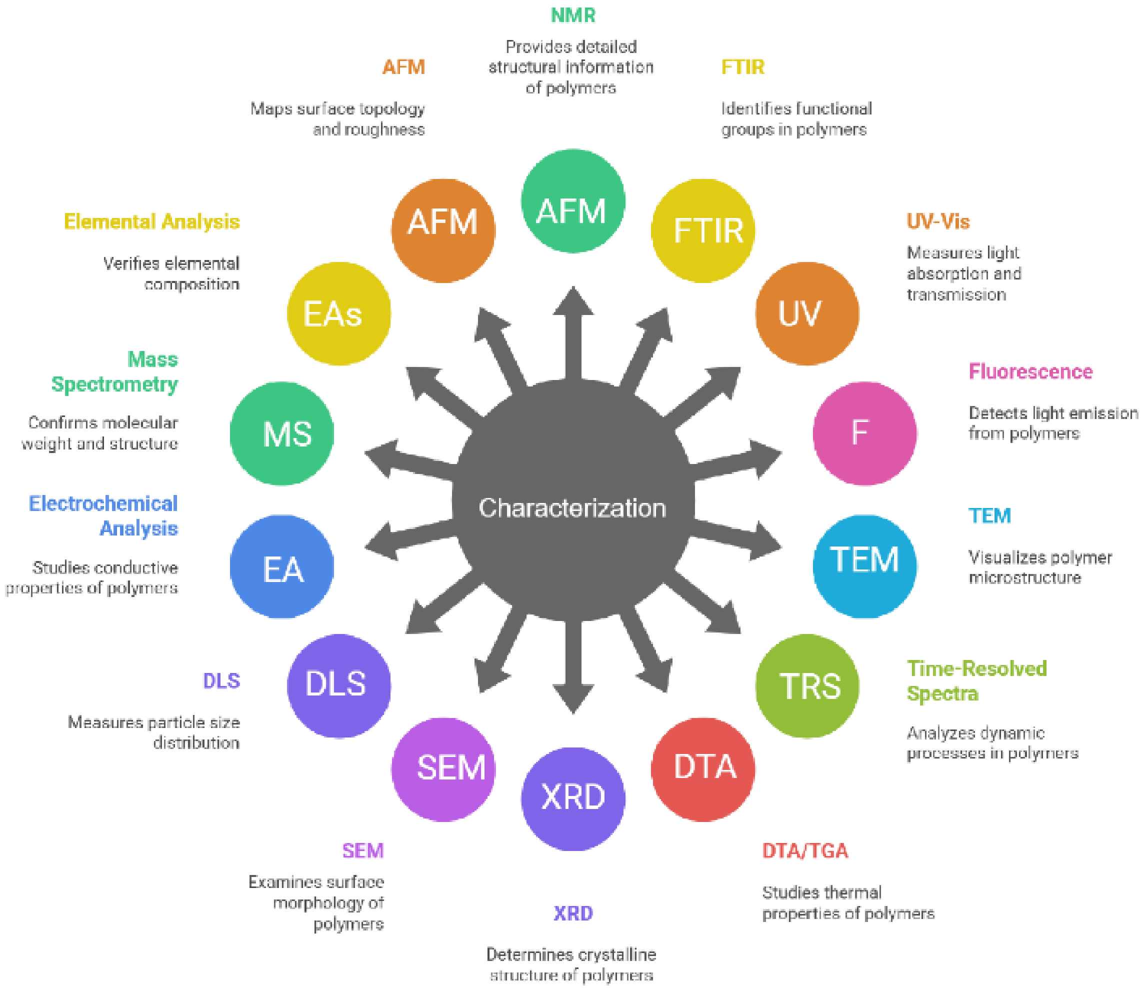

Figure 3. Characterization techniques of polymers.

3. Members of aromatic amines

Polymers and oligomers with extended π-conjugated systems are commonly called "conjugated polymers" or "conjugated oligomers." These materials are made of regularly repeating units with alternating single and double bonds. Often, heteroatoms such as nitrogen, oxygen, and sulfur, which have lone electron pairs, participate in conjugation by interacting with neighboring π-orbitals, helping form an extended poly-conjugated system [7, 8]. The high level of electron delocalization along the polymer backbone results in a variety of unique physicochemical properties. As a consequence, conjugated polymers show electronic and optical activity, resistance to radiation, semiconducting behavior, paramagnetism, and catalytic functions, making them essential for developing sensors and detectors [52–54], polymer batteries [55–57], semiconductor diodes [10, 58], solar cells [59], and various biomedical devices [60–62].

Polyaromatic amines, specifically, are high-molecular-weight compounds with a conjugated bond system and a nitrogen atom with a lone electron pair incorporated into the aromatic ring. The synthesis of these polymers and oligomers-widely used across various technological fields due to their distinctive properties-along with understanding their composition, structure, and functional features, is a complex yet fascinating area of research.

3.1 Historical background of Aniline

The history of the oxidative polycondensation of aniline - the first and most fundamental aromatic amine - begins in the early 19th century. Aniline is an organic compound originally derived from coal tar. The German chemist Otto Unverdorben first isolated it from indigo dye in 1826 and named it "crystallin" [63], although its chemical structure was unknown at the time. In 1835, Friedlieb Ferdinand Runge isolated another coal-tar substance called "kyanol" (or "cyanol"), which turned a vivid blue when treated with calcium hypochlorite. The word "kyanol," rooted in the Greek kuanos (blue) and Latin oleum (oil), actually referred to aniline [4]. The first person to officially name the substance "aniline" (from anil, the Spanish name for indigo) was Karl Julius Fritzsche, who obtained it by treating indigo with caustic potash in 1840 [5]. During his studies of coal-tar distillation, Runge also discovered pyrrole and quinoline. Notably, he observed that aniline formed insoluble, variably colored solids when exposed to different oxidizing agents. In one experiment, he added hydrochloric acid to a porcelain cup containing gold oxide and a few drops of aniline, then heated the mixture to 100 °C. This produced a violet material that turned blue-gray upon drying. Two years later, in 1842, Nikolai Nikolaevich Zinin synthesized the same substance by reducing nitrobenzene and called it "benzydam" [64]. In 1843, August Wilhelm von Hofmann (1818–1892) demonstrated that Unverdorben's "crystallin," Runge's "kyanol," Fritzsche's "aniline," and Zinin's "benzydam" were actually identical compounds, confirming the true identity of aniline, later known as phenylamine or simply aniline [13, 64, 65]. Fritzsche also reported that aniline first turns yellow, then brown, upon exposure to air. Under certain conditions, reacting with nitrous acid (HNO_2) produces blue or green products. Treating aniline salts with chromic acid (H_2CrO_4) results in a dark green precipitate that later turns blue-black. In 1853, Beissenhirz showed that aniline produces a blue color when exposed to concentrated sulfuric acid and potassium dichromate. However, none of these early scientists managed to turn their discoveries into commercial applications.

In the mid-19th century, chemists began exploring the potential of aniline as a dye for textiles. Their investigations demonstrated that aniline and its derivatives could generate a wide spectrum of colors. In 1860, Crace-Calvert, Samuel Clift, and their assistant Charles Lowe obtained green and blue cotton dyes by oxidizing aniline, for which they received a joint patent the same year [66, 67]. A prolonged, 12-hour reaction of aniline salts with potassium chlorate yielded a green product known as "emeraldine," a name that later became widely associated with aniline derivatives. When this material was boiled in an alkaline or soapy medium, it converted into a blue substance referred to as "azurine"[68].

Lightfoot [67] demonstrated that only a small amount of potassium chlorate was required to oxidize aniline salts; however, achieving an intense coloration required an additional oxidizing agent, such as copper [66]. The use of copper salts caused corrosion, leaving marks on printed fabrics. This problem was resolved by Charles Louth in 1864, who introduced copper sulfide as an alternative. Because copper sulfide is insoluble, it remained inactive during the printing process, and only after aniline black was formed did the chlorate convert it into copper sulfate, significantly reducing damage to printing cylinders [68, 69].

Around the same period, in 1860, Heinrich Caro synthesized the second black aniline dye. Caro later supervised the production of numerous new dyes, including artificial alizarin, eosin, methylene blue, and several azo dyes. He also contributed to early studies on indigo synthesis and helped elucidate the structures of triphenylmethane dyes [69, 70]. In 1863, Charles Louth and August Wilhelm von Hofmann oxidized aniline hydrochloride with potassium dichromate, producing a deep black pigment known as aniline black - one of the first synthetic black dyes. Its intense coloration, washfastness, and ease of application led to its rapid adoption in the textile industry.

The discovery of aniline black marked a major milestone in the transition from natural to synthetic dyes and stimulated extensive research into aniline-based pigments. This work laid the foundation for synthetic dye chemistry and enabled the development of a broad palette of artificial colors still used today. Following this breakthrough, a significant contribution was made by the physician and chemist Henry Letheby [15], who, while investigating nitrobenzene poisoning, discovered that nitrobenzene is metabolically reduced to aniline. This finding prompted the development of early chemical tests for detecting aniline [71].

Subsequent studies established that the highest-quality aniline black is obtained by oxidizing aniline salts-typically using HCl or H_2SO_4 as the reaction medium, in the presence of strong inorganic oxidants such as dichromates or chlorates and catalysts including $CuSO_4$ or $Fe(CH_3COO)_2$ at temperatures of 333–373 K [72].

In the 1870s and 1880s, Adolf Baeyer and several other chemists made significant scientific advances in collaboration with Caro and leading industrial researchers. Baeyer contributed to the understanding of tautomerism and proposed the modern structural formula for indigo. Although technical challenges-particularly those related to synthesizing indigo from inexpensive starting materials-remained unresolved for many years, major progress toward artificial indigo production resulted from Baeyer's research, initiated in 1865 at the Berlin Institute of Chemistry and supported by Caro during the mid-1870s [12].

Following these discoveries, a distinct group of electroactive materials known as intrinsically conductive polymers (ICPs) emerged. Achieving high conductivity in these polymers typically requires doping, which increases the density of mobile charge carriers. Among the various ICPs, polyaniline (PANI) is one of the most intensively studied. PANI stands out due to its straightforward synthesis, low cost, versatile redox behavior, and the ability to undergo reversible doping and dedoping through simple acid–base reactions. It also offers greater chemical and environmental stability than many other conductive polymers. Nevertheless, PANI still encounters persistent challenges related to poor solubility and limited processability, largely resulting from the rigidity of its conjugated backbone. These issues have constrained its widespread technological deployment, prompting continued research aimed at improving its solubility and processability.

A major advancement in this field was the introduction of copolymerization strategies involving aniline and structurally compatible monomers. Self-doped polyaniline derivatives produced through these approaches exhibit substantial improvements, including enhanced solubility, greater flexibility, and more stable redox and conductivity behavior across a wide pH range. Numerous comonomers containing functional groups such as $-OH$, $-NH_2$, $-SO_3H$, and $-COOH$ etc., have been incorporated to achieve intrinsic doping, increase processability, and tailor the electronic properties of the resulting materials. In recent years, considerable research attention has been devoted to the synthesis and physicochemical characterization of aniline-based copolymers and their derivatives using a variety of polymerization techniques.

As a result, a series of soluble, thermally stable, flexible, and multifunctional copolymers/co-oligomers have been successfully synthesized from aniline and a range of versatile monomers. These materials exhibit improved processability, enhanced mechanical integrity, and tunable physicochemical properties owing to the incorporation of functional groups introduced through copolymerization. Owing to their conjugated structures and adjustable electronic behavior, such polymers find broad application in Optoelectronic Devices, including use in coating technologies, chemical and electrochemical sensors, rechargeable battery components, supercapacitors, flexible electronics, and other advanced functional devices.

3.2 Methyl aniline (o-Toluidine)

O-Toluidine (2-aminotoluene or *o*-methylaniline), a methyl-substituted derivative of aniline, has been an important compound in the evolution of synthetic organic chemistry and the early dye industry. Its history extends over nearly two centuries and reflects the rapid industrial and scientific developments of the 19th century. The compound was first conclusively identified in 1845, when James Sheridan Muspratt and August Wilhelm von Hofmann characterized *o*-toluidine alongside its *m*- and *p*-isomeric forms. Their work built upon earlier studies of coal-tar–derived aniline derivatives, which were becoming significant industrial raw materials at the time.

The commercial relevance of *o*-toluidine became apparent with the emergence of the first synthetic organic dyes. Landmark colorants such as mauveine and fuchsine marked the beginning of the synthetic dye industry, and *o*-toluidine soon became a key precursor in the manufacture of these early "aniline dyes." Its chemical reactivity and propensity to form intensely colored oxidation products made it a valuable intermediate for large-scale dye production.

By 1880, the increasing demand for toluidine-based dyes led to the establishment of commercial *o*-toluidine production in the United Kingdom. This development positioned *o*-toluidine as an important industrial building block in the synthesis of dyes, pigments, pharmaceuticals, and various polymeric materials, while also facilitating the broader adoption of coal-tar chemistry in industrial practice.

Following the discovery of intrinsically conductive polymers (ICPs), interest in aniline and its derivatives grew significantly. These compounds have been extensively studied because of their ability to polymerize in various media and copolymerize with a wide range of monomers. O-Toluidine, in particular, has frequently been used in copolymerization reactions to create materials with customized structural and electronic properties. The resulting homopolymers, copolymers, and their oligomeric counterparts have applications in sensors, energy storage devices, electronic components, and protective coatings.

3.3 Ortho-phenylenediamine

The story of phenylenediamine polymers has to be started with polyaniline. Phenylenediamine is the common name for diaminobenzene, which exists as three isomers: 1,2-, 1,3-, and 1,4-diaminobenzene. The 1,2-isomer is commonly called o-phenylenediamine; the 1,3-isomer is m-phenylenediamine; and the 1,4-isomer is p-phenylenediamine. O-phenylenediamine (o-PDA or 1,2-benzenediol), containing two amino groups in the 1st and 2nd positions, has been used as a precursor for heterocycles, dyes, and pharmacologically active molecules since the late 19th century. Initially, these compounds were obtained by reducing substances such as o-dinitrobenzene and o-nitroaniline [73]. Its importance increased in the 20th century with the development of benzimidazole chemistry and the subsequent development of POPD by oxidation-polycondensation, which allowed the production of redox-active films for electronic and electroanalytical applications [74, 75]. Poly-ortho-phenylenediamine (p-OPD) has been synthesized mostly chemical and electrochemical methods [76, 77].

In chemical synthesis, OPD is typically polymerized by exposing its solution to an appropriate oxidant, reductant, or initiator, leading to the formation of polymeric materials in either powder or thin-film form. Common oxidizing agents employed in OPD polymerization include $K_2Cr_2O_7$, $FeCl_3$, $K_2S_2O_8$, $(NH_4)_2S_2O_8$, and H_2O_2. Extensive studies have utilized this chemical oxidative polymerization approach to produce and characterize poly(o-phenylenediamine) and its derivatives [78].

In electrochemical polymerization, redox-active units may be incorporated directly into the growing polymer backbone, added as pendant substituents through pre-functionalized monomers, or introduced in a separate post-functionalization step after film deposition. Poly(o-phenylenediamine) (POPD) was first obtained as a robust and adherent coating on electrode surfaces by electropolymerizing OPD in acidic media [19]. Since the mid-1980s, extensive studies have explored the electro-polymerization behavior of aromatic diamines. Importantly, POPD films generated via cyclic voltammetry display IR absorption patterns distinct from those produced under potentiostatic conditions [79, 80]. Moreover, polymers synthesized electrochemically exhibit NMR characteristics that differ noticeably from POPD obtained through conventional chemical oxidative methods. Copolymerization offers an effective route to functionalize OPD and tailor its photo-physical, optical, and structural characteristics [75, 76, 81]. Numerous studies have demonstrated that combining OPD with other conducting or semiconducting monomers-acting as donor or acceptor units-can significantly modify and improve the resulting material’s properties. The wide range of possible co-monomers and the freedom to adjust their ratios provide a versatile platform for designing OPD-based nanomaterials with enhanced physical, optical, and performance attributes. The composition of the monomer feed, along with reaction parameters such as temperature, catalyst, and medium pH, plays a decisive role in determining the structural and functional characteristics of the resulting co-polymer [75, 77].

POPD and its copolymers have been applied in a broad range of fields, including electrode materials[82], optoelectronic and solar cells [83], anode materials for lithium-ion batteries [84], sensors [85], supercapacitors [86, 87], anticorrosion coatings [88], and the removal of Cd(II) from aqueous solutions [89], etc.

Despite its broad range of applications, OPD and its polymers exhibit several limitations. The monomer is intrinsically toxic and therefore requires careful handling. Poly(o-phenylenediamine) also suffers from low solubility and only moderate conductivity relative to polyaniline. Furthermore, oxidative polymerization often produces heterogeneous structures and variations in color, and some formulations show limited mechanical flexibility. Ongoing research aims to address and overcome these drawbacks.

3.4 Metha-phenylenediamine

Metha-Phenylenediamine (m-PDA or 1,3-diaminobenzene), one of the three phenylenediamine isomers, has been recognized as an important intermediate in dye chemistry and early polymer science since the late 19th century. Historically, it served as a key precursor for azo dyes, photographic developers, and rubber antioxidants. Industrially, m-PDA is produced by catalytic hydrogenation of 1,3-dinitrobenzene - the principal product obtained from the dinitration of benzene using sulfuric–nitric acid mixtures. This hydrogenation step is typically carried out in water or methanol over supported palladium catalysts or Raney nickel [90]. Over time, m-PDA is used in several industrially significant sectors:

a. High-performance polymers: – m-PDA is a critical monomer in the synthesis of aramids, such as poly(m-phenyleneterephthalamide), and in high-temperature polyimides, poly(amide-imide) s, and heteroaromatic frameworks [91, 92]. Examples are protective clothing and aircraft interiors. The polymer is made in the United States by Du Pont (Nomex), in Japan by Teijin, and in the former Soviet Union. The m-PDA is also used for curing epoxy resins to impart high-temperature strength and good resistance to chemical solvents. Such cured resins are used in filamentwound casings and adhesives. m-PDA is still used as the starting material for many dyes. Examples include Basic Brown 1 (Bismarck Brown), Basic Orange 2, Direct Black 38, and Developed Black BH [93, 94].

b. Conducting and electroactive materials : - m-PDA plays a significant role in the development of conducting and electroactive materials due to its bifunctional amine groups and rigid aromatic backbone, which facilitate electron delocalization and redox activity [95]. It is widely employed in the synthesis of aromatic poly(amine) frameworks, redox-active oligomers, and electrochemically responsive thin films. These materials often exhibit tunable conductivity, reversible redox behavior, and strong adhesion to various substrates, contributing to their utility in sensors, anticorrosion coatings, and electronic devices [96].

In addition, m-PDA readily participates in oxidative polymerization and metal-coordination reactions, enabling the formation of electrocatalytic films and metal - organic hybrid materials with enhanced electron-transfer properties[52]. Recent studies have emphasized its potential as a monomer for heat-resistant conductive polymers, organometallic complexes exhibiting high catalytic activity, and advanced composite materials that combine mechanical stability with improved electrical or electrochemical performance [95]. The structural versatility and redox behavior of m-PDA continue to support innovations in energy-storage materials, electrocatalysis, and functional protective coatings.

c. Dyes and pigments : - It serves as an intermediate for azo dyes, developer agents, and hair-color formulations [73].

d. Corrosion inhibitors : - m-PDA acts as a corrosion inhibitor through adsorption on metal surfaces and formation of protective films.

e. Pharmaceuticals and fine chemicals : - It is a precursor to numerous heterocycles and medicinal intermediates.

f. Nanomaterials and adsorbents : - m-PDA is used for synthesizing functional nanoparticles, carbon dots, and polymer-based adsorbents for water purification [97].

Limitations - Despite its wide utility, m-PDA presents several limitations. It is classified as harmful and a skin sensitizer, requiring regulated handling. The compound oxidizes readily in air, forming quinonoid species that change color and alter reactivity. Solubility limitations and undesirable color formation complicate its use in optical or transparent systems. Additionally, the highly reactive amine groups may lead to rapid crosslinking or uncontrolled branching in polymer synthesis.

Conclusion

m-Phenylenediamine is a versatile aromatic diamine with broad impact across polymer science, dye chemistry, and materials engineering. Its rigid aromatic core and reactive amine groups enable the formation of high-performance polymers, functional coatings, and advanced nanomaterials. Although challenges remain - including toxicity, oxidative instability, and processing difficulties - ongoing advances in green chemistry, controlled polymerization, and functional material design continue to expand the relevance of m-PDA in modern research and applications.

3.5 Para-phenylenediamine

Para-phenylenediamine (p-PDA), one of the three phenylenediamine isomers (in 1,4- postions), has been known since the late 19th century. The p-PDA is a crystalline solid that can appear in various colors, including pink, gray, yellow, or even colorless. Upon exposure to air, it undergoes oxidation, first turning red, then brown, and finally black. Many sources state that p-PDA was first synthesized by August Wilhelm von Hofmann in 1863, who was notably the chemistry professor of William Henry Perkin, the discoverer of the world's first synthetic dye, mauve (MOTM, January 1996) [98]. It was initially used as an intermediate for azo dyes and as a photographic developer, reducing silver halides to metallic silver under alkaline conditions, with its oxidation products exploited in dye formation. The industrial synthesis of p-PDA takes place in two steps: dinitration of benzene and catalytic hydrogenation of dinitrobenzene. Early applications also included rubber antioxidants and vulcanization accelerators. Its bifunctional amine groups and rigid para-substituted aromatic structure later made p-PDA a key monomer for wide range of polymers [99–101]. Over time, it has remained an important building block in organic synthesis, high-performance polymers such as aramids and poly-ureas, dyes and pigments, photographic and electronic applications, rubber, coatings, and other related fields [43, 73, 102–104].

Despite its broad range of applications, p-PDA also presents several limitations. It is a well-known skin sensitizer and allergen, and exposure through inhalation or ingestion poses health risks, leading to strict regulatory restrictions. Similar to other aromatic diamines, p-PDA readily oxidizes in air to form quinonoid species, which can affect its color, reactivity, and overall storage stability. Furthermore, its moderate solubility in organic solvents and highly reactive amine groups require careful handling to avoid unintended crosslinking during polymer processing.

4. Potential application of polymers

Aromatic amine-based polymers are an important class of conjugated and functional polymers with diverse technological applications (Figure 4). Their rich redox chemistry, environmental stability, tunable electronic structure, and ability to incorporate diverse substituents make them useful in a number of modern materials systems.

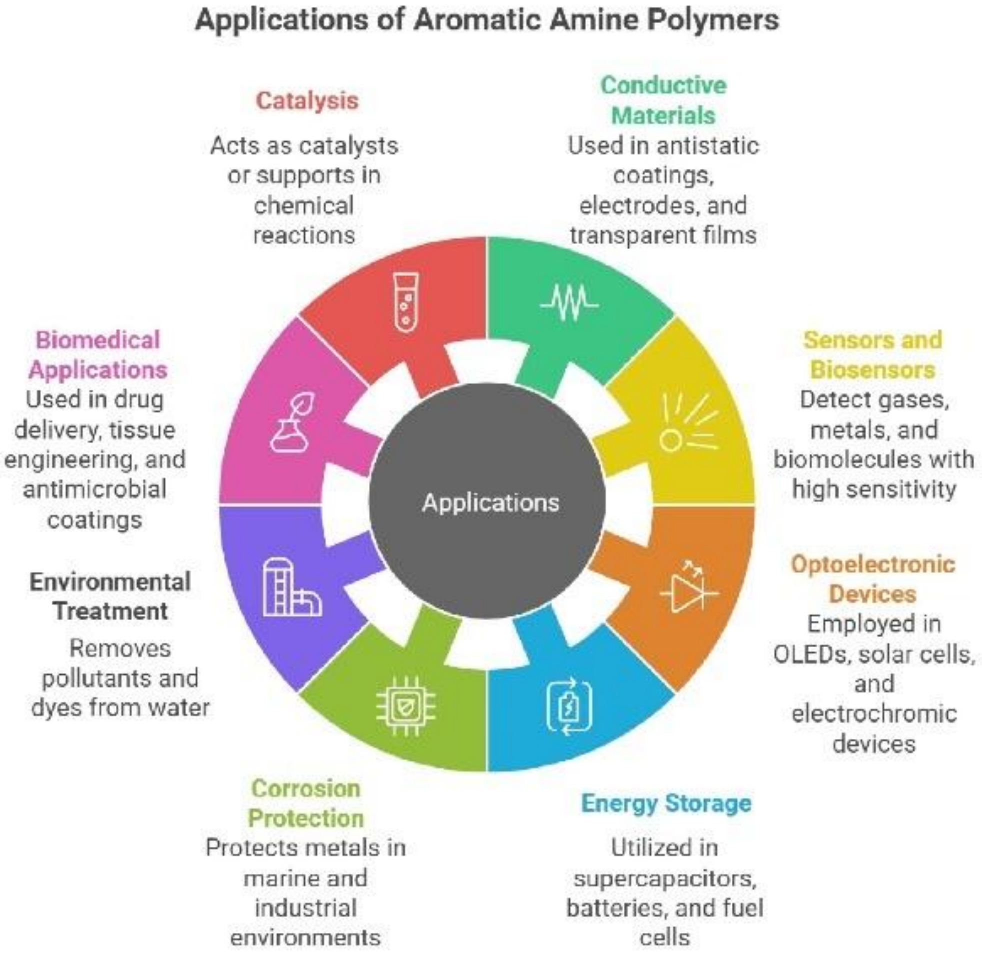

Figure 4. Applications of polymers based on aromatic amines monomers.

Conclusion

Although aromatic amines have been investigated for more than a century, compounds such as aniline and the diaminobenzenes continue to attract significant scientific attention. Polyaniline, for instance, was originally used as a dye but later emerged as one of the most extensively studied conducting polymers, finding applications in electronics, sensors, energy storage, anticorrosion coatings, and other advanced technologies. To enhance its physicochemical properties - including stability, solubility, and processability - researchers have widely explored the copolymerization of aniline with various monomers.

Compared with aniline, aromatic diamines (o-PDA, m-PDA, p-PDA) received scientific interest somewhat later, yet their importance has grown substantially over the past several decades. While their early use was largely limited to dye and pigment manufacture, the homo- and copolymers derived from these diamines are now employed across a broad range of modern technological fields, including optics, optoelectronics, sensing devices, smart and responsive materials, anticorrosion coating, semiconductor applications and etc. Their bifunctional amine groups, ability to form highly conjugated structures, and capacity for metal coordination further expand their utility in advanced materials.

Nevertheless, despite their valuable mechanical, electronic, and chemical characteristics, several intrinsic properties of aromatic amines - such as oxidative instability, toxicity, limited solubility, and high reactivity - continue to restrict their wider application and require careful management in both research and industrial setting.

Currently, researchers are pursuing various strategies to overcome these limitations and improve the performance of aromatic amine–based materials.

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Conflict of Interest

The authors declare no conflict of interest.

REFERENCES

1. Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa*, H., Louis, E. J., Gau, S. C., MacDiarmid, A. G. (1977). Electrical Conductivity in Doped Polyacetylene. *Phys. Rev. Lett,* 39(17), 1098–1101. DOI: **DOI.**org/10.1103/PhysRevLett.39.1098
2. Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa*, H., Louis, E. J., MacDiarmid, A. G.. (1978). Conducting polymers: Halogen doped polyacetylene. *J. Chem Phys, 69*(11), 5098–5104. **DOI.**org/10.1063/1.436503
3. MacDiarmid, A. G. (1997). Polyaniline and polypyrrole: Where are we headed? Synth Met, *84*(1-3), 27–34. **DOI.**org/10.1016/S0379-6779(97)80658-3
4. Macdiarmid, A. G., Heeger, A. J. (1979). Organic Metals and Semiconductors: The Chemistry of Polyacetylene, (CHX, And Its Derivatives. *Synthetic Metals, 1*(2), 101-118. **DOI**.org/10.1016/0379-6779(80)90002-8
5. Chiang, J. C., Macdiarmid, A. G. (1986). Polyaniline: Protonic Acid Doping of the Emeraldine form to the Metallic Regime. *Synthetic Metals, 13*(1-3), 195-205. **DOI.**org/10.1016/0379-6779(86)90070-6
6. Heeger, A. J. (2001). Semiconducting and metallic polymers: the fourth generation of polymeric materials. *J Phys Chem B, 105*(36), 8475–8491. **DOI.**org/10.1021/jp011611w
7. Gerhard Koßmehl. (1979). Semiconductive Conjugated Polymers. *Berichte der Bunsengesellschaft für physikalische Chemie,* 83(4), 417–426. **DOI.**org/10.1002/bbpc.19790830422
8. Brédas, J. L., Elsenbaumer, R. L., Chance, R. R., Silbey, R. (1983). Electronic properties of sulfur containing conjugated polymers. *J Chem Phys, 78*, 5656–5662. **DOI**.org/10.1063/1.445447
9. Reynolds JRTBCSTA (2019). Conjugated Polymers, 4th Edition. CRC Press, Boca Raton
10. Jadoun S, Riaz U (2020). Conjugated Polymer Light-Emitting Diodes. In: Polymers for Light-Emitting Devices and Displays. Wiley, pp 77–98. **DOI:**10.1002/9781119654643.ch4
11. Ganachari, S.V., Mogre, P., Tapaskar, R.P., Yaradoddi, J.S., Banapurmath, N. R. (2018). Polyaniline Synthesis and Its Wide-Range Sensor and Electronic Applications. Springer International Publishing 1267–1292. https://doi.org/10.1007/978-3-319-68255-6_186
12. Antony, S.T. (2009). Anilines: Historical Background. In: Patai's Chemistry of Functional Groups. Wiley, 1-73. **DOI.**org/10.1002/9780470682531.pat0383
13. Fritsche, J. (1840). Ueber das Anilin, ein neues Zersetzungsproduct des Indigo. *J. Fritzsche*, *36*(1), 84–90. **DOI:**10.1002/jlac.18400360108
14. M. Probst RH (1997). A systematic spectroelectrochemical investigation of alkyl substituted anilines and their polymers. *Macromol Chem Phys,* 198, 1499–1509.
15. Poddar, A., Patel, S.S., Patel, H.D. (2021). Synthesis, characterization and applications of conductive polymers: A brief review. *Polym Adv Technol,* 32(12), 4616–4641. **DOI.**org/10.1002/pat.5483

16. Rzayev, R.S., Mammadov, B.A., Abdullayev, Y.F., Ibadov, E. A. (2022). Synthesis and characterization of new nano-sized poly(p-phenylenediamine) in the presence of potassium persulfate. *Processes of Petrochemistry and oil Refining (PPOR),* 23(2),495–509.
17. Rzayev, R., Sucman, N., Geru, I., et al. (2025). Synthesis and Characterization of Nano-Sized Poly-(1,4-Diaminonaphthalene) in Potassium Persulfate. *Acta Chim Slov,* 72, 260–268. **DOI.**org/10.17344/acsi.2024.9032
18. Mortimer, R.J. (1995). Spectroelectrochemistry of electrochromicpoly(o-toluidine) and poly(m-toluidine) films. *J Mater Chem*, 5, 969–973. **DOI.**org/10.1039/JM9950500969
19. Maiyalagan, T. (2008). Electrochemical synthesis, characterization and electro-oxidation of methanol on platinum nanoparticles supported poly(o-phenylenediamine) nanotubes. *J Power Sources,* 179, 443–450. **DOI.**org/10.1016/j.jpowsour.2008.01.048
20. Geise, R. J. Adams, J. M., Barone, N, J., Yacynych, A. M. (1991). Electropolymerized films to prevent interferences and electrode fouling in biosensors. *Biosens Bioelectron, 6(*2),151–160. **DOI:**10.1016/0956-5663(91)87039-e
21. Sipahi, M., Parlak, A. E., Gul, A., Ekinci, E., Yard;m, M.F., Sarac, A.S. (2008). Electrochemical impedance study of polyaniline electrocoated porous carbon foam. *Prog Organic Coatings, 62,* 96–104. **DOI.**org/10.1016/j.porgcoat.2007.09.023
22. Buzarovska, A., Arsova, I., Larsov, L. (2001). Electrochemical synthesis of poly-(2-methyl aniline): electro-chemical and spectroscopic characterization. *Journal of the Serbian Chemical Society,* 66(1), 27–37. **DOI:**10.2298/JSC0101027B
23. Shan, J., Han, L., Bai, F,. Cao, Sh. (2003). Enzymatic polymerization of aniline and phenol derivatives catalyzed by horseradish peroxidase in dioxane (II). *Polym Adv Technol,* 14(3-5), 330–336. **DOI:**10.1002/pat.316
24. Kaya, İ., Yağmur, H. (2021). Synthesis of poly(4-aminosalicylic acid) through enzymatic and oxidative polycondensation by H_2O_2 oxidant. *Iranian Polymer Journal, 31,* 199–214. **DOI.**org/10.1007/s13726-021-00990-1
25. Alva, K. Shridhara., Kumar, Jayant., Marx, Kenneth A., Tripathy, S. K. (1997). Enzymatic synthesis and characterization of a novel water-soluble polyaniline: poly (2,5-diaminobenzenesulfonate). *Macromolecules,* 30, 4024–4029. **DOI.**org/10.1021/ma961544h
26. Cruz-silva, R., Escamilla, A., Nicho, M. E, et al. (2007). Enzymatic synthesis of pH-responsive polyaniline colloids by using chitosan as steric stabilizer. *European Polymer Journal,* 43(8), 3471–3479. **DOI.**org/10.1016/j.eurpolymj.2007.05.027
27. Kaya, I., Yağmur, H. K. (2020). Synthesis and characterization of poly-(3,5-diaminobenzoic acid) via enzymatic and oxidative polymerization and application in methylene blue adsorption. *J Mol Struct,* 1216, 128323. **DOI.**org/https://doi.org/10.1016/j.molstruc.2020.128323
28. Tonami, H., Uyama, H., Kobayashi, S., Reihmann, M. (2002). Enzymatic polymerization of m -substituted phenols in the presence of 2, 6-di-O-methyl-β-cyclodextrin in water. *e-Polymers*, 1–7. **DOI.**org/10.1515/epoly.2002.2.1.46
29. Cruz, G. J., Morales, J., Castillo-Ortega, M.M., Olayo, R. (1997). Synthesis of polyaniline films by plasma polymerization. *Synthetic Metals, 88(3),* 213-218. **DOI.**org/10.1016/S0379-6779(97)03853-8
30. Abdiryim, T., Jamal, R., Nurulla, I. (2007). Doping effect of organic sulphonic acids on the solid-state synthesized polyaniline. *J Appl Polym Sci,* 105, 576–584. **DOI.**org/10.1002/app.26070
31. Jamal, R., Abdiryim, T., Nurulla, I. (2008). Comparative studies of solid-state synthesized poly(o-methoxyaniline) and poly (o-toluidine). Polym Adv Technol, 19(11), 1461–1466. **DOI.**org/10.1002/pat.1139
32. Behzadi, M., Noroozian, E., Mirzaei, M. (2013). A novel coating based on carbon nanotubes/poly-ortho-phenylenediamine composite for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons. *Talanta, 108,* 66–73. **DOI.**org/10.1016/j.talanta.2013.02.040
33. Kubota, M. M., Sacco, B. L., Bento, D.C., Santana, H. De. (2015). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy Synthesis and spectroscopic analysis of polydiphenylamine via oxidation with bentonite clay in the solid state. *Spectrochim Acta A Mol Biomol Spectrosc, 151,* 80–88. **DOI.**org/10.1016/j.saa.2015.06.092
34. Hongjin, Q., Wan, M., Matthews, B., Dai, L. (2001). Conducting Polyaniline Nanotubes by Template-Free Polymerization. *Macromolecules, 4,* 675–677. **DOI.**10.1021/ma001525e
35. Wu, J., Zhou, D., Looney, M. G., Too, C.O. (2009). A molecular template approach to integration of polyaniline into textiles. *Synthetic Metals, 159,* 1135–1140. **DOI.**org/10.1016/j.synthmet.2009.01.054
36. Jin, X., Yu, L., Zeng, X. (2008). Chemical Enhancing the sensitivity of ionic liquid sensors for methane detection with polyaniline template. *Sensors and Actuators B, 133,* 526–532. **DOI.**org/10.1016/j.snb.2008.03.022

37. Xian, Y., Liu, F., Feng, L., Wu, F., Wang, F., Jin, L. et al (2007) Nanoelectrode ensembles based on conductive polyaniline/poly (acrylic acid) using porous sol–gel films as template. *ScienceDirect,* 9, 773–780. **DOI.**org/10.1016/j.elecom.2006.11.017
38. Ferreira, A. A., Sanches, E. A. (2017). Multimorphologies of hydrochloride polyaniline synthesized by conventional and interfacial polymerization. *J Mol Struct, 1143,* 294–305. **DOI**.org/10.1016/j.molstruc.2017.04.104
39. Dallas, P., Stamopoulos, D., Boukos, N., Tzitzios, V., Niarchos, D., Petridis, D. (2007). Characterization, magnetic and transport properties of polyaniline synthesized through interfacial polymerization. *Polymer (Guildf),* 48, 3162–3169. https://doi.org/10.1016/j.polymer.2007.03.055
40. Kuo, C. W, Wen, T. C. (2008). Dispersible polyaniline nanoparticles in aqueous poly-(styrenesulfonic acid) via the interfacial polymerization route. *Eur Polym J,* 44, 3393–3401. **DOI.**org/10.1016/j.eurpolymj.2008.07.018
41. Dallas, P., Georgakilas, V. (2015). Interfacial polymerization of conductive polymers: Generation of polymeric nanostructures in a 2-D space. *Adv Colloid Interface Sci, 224*, 46–61. **DOI.**org/10.1016/j.cis.2015.07.008
42. Detsri, E., Dubas, S. T. (2009). Interfacial Polymerization of Water-Soluble Polyaniline and Its Assembly Using the Layer-By-Layer Technique. *J Metals, Materials and Minerals,19*, 39-44.
43. Soltane, L., Sediri, F. (2013). Hydrothermal synthesis, characterization and electrical investigation of poly (para-phenylenediamine) / vanadium oxide nanocomposite nanosheets. *Materials Science & Engineering B*, 178, 502–510. **DOI.**org/10.1016/j.mseb.2013.02.005
44. Lakouraj, M. M., Zare, E. N., Moghadam, P. N. (2014). Synthesis of novel conductive poly(p-phenylenediamine)/ Fe 3O4 nanocomposite via emulsion polymerization and investigation of antioxidant activity. *Advances in Polymer Technology* 33, 1-7. **DOI.**org/10.1002/adv.21385
45. Palaniappan, S., Jhon, A. (2008). Polyaniline materials by emulsion polymerization pathway. *Prog Polym Sci* 33, 732–758. **DOI.**org/10.1016/j.progpolymsci.2008.02.002
46. Jadoun, S., Verma, A., Ashraf, S. M., Riaz, U. (2017). A short review on the synthesis, characterization, and application studies of poly(1-naphthylamine): a seldom explored polyaniline derivative. *Colloid Polym Sci*, 295, 1443–1453. **DOI**.org/10.1007/s00396-017-4129-2
47. Jadoun, S., Riaz, U., Yáñez, J., Chauhan, N. P.S. (2021). Synthesis, characterization and potential applications of Poly(o-phenylenediamine) based copolymers and Nanocomposites: A comprehensive review. *Eur Polym J,* 156, 110600. **DOI.**org/10.1016/j.eurpolymj.2021.110600
48. Chauhan, R. P, Kumar, R., Chakarvarti, S.K. (2010). Synthesis of conducting polymers and their characterization. *Indian Journal of Pure and Applied Physics,* 48(7), 524–526.
49. Dumitrescu, I., Nicolae, C-A., Mocioiu, A.M., Gabor, R.A., Grigorescu, M., Mihailescu, M. (2009). Synthesis and characterization of conductive polymers with enhanced solubility. *UPB Sci Bull, Series A, 71,* 63–72.
50. Grigoras, M., Antonoaia, N-C. (2005). Synthesis and characterization of some carbazole-based imine polymers. *Eur Polym J,* 41,1079–1089. **DOI:**10.1016/j.eurpolymj.2004.11.019
51. Yağmur, H. K., Kaya, I. (2020). Synthesis and characterization of new polymers derived from 2-methyl-m-phenylenediamine as an effective adsorbent for cationic dye removal. *Arabian Journal of Chemistry,* 13, 8183–8199. **DOI.**org/10.1016/j.arabjc.2020.09.052
52. Dube, A., Malode, S. J., Alodhayb, A. N., et al. (2025). Conducting polymer-based electrochemical sensors: Progress, challenges, and future perspectives. *Talanta Open,* 11, 100395. **DOI.**org/10.1016/j.talo.2024.100395
53. Baranwal, J., Barse, B., Gatto, G., Broncova, G., Kumar, A. (2022). Electrochemical Sensors and Their Applications: A Review. *Chemosensor*, 10(9), 363. **DOI.**org/10.3390/chemosensors10090363

54. Bai, H., Shi, G. (2007). Gas sensors based on conducting polymers. *Sensors*, 7, 267–307. **DOI.**org/10.3390/s7030267
55. Chen, Ch., Gan, Z., Xu, Ch., Lu, L., Liu, Y., Gao, Y. (2017). Electrosynthesis of poly(aniline-co-azure B) for aqueous rechargeable zinc-conducting polymer batteries. *Electrochim Acta,* 252, 226–234.
56. Bahceci, S., Esat, B. (2013). A polyacetylene derivative with pendant TEMPO group as cathode material for rechargeable batteries. *J Power Sources,* 242, 33–40. **DOI.**org/10.1016/j.jpowsour.2013.05.051
57. Costa, C.M., Lizundia, E., Lanceros-Méndez, S. (2020). Polymers for advanced lithium-ion batteries: State of the art and future needs on polymers for the different battery components. *Prog Energy Combust Sci*, 79, 100846. **DOI.**org/10.1016/j.pecs.2020.100846

58. Karg, S., Scott, J.C., Salem, J.R., Angelopoulos, M. (1996). Increased brightness and lifetime of polymer light-emitting diodes with polyaniline anodes. *Synth Met,* 80, 111–117.
59. Get, R., Islam, Sk. M., Sing, S., Mahala, P. (2020). Organic Polymer Bilayer Structures for Applications in Flexible Solar Cell Devices. *Microelectron Eng,* 222, 111200. **DOI.**org/doi:10.1016/j.mee.2019.111200
60. Toktam Nezakati ASAT and AMSeifalian (2018). Conductive Polymers: Opportunities and Challenges in Biomedical Applications. *Chem Rev,* 118, 6766–6843. **DOI:**10.1021/acs.chemrev.6b00275
61. Du, A., Liu, Sh., Li, Y. (2025). Hollow Conductive Polymer Nanospheres with Metal–Polyphenol Interfaces for Tunable Hydrogen Peroxide Activation and Energy Conversion. *Polymers, 17*(24), 3305. **DOI.**org/10.3390/polym17243305
62. Zhang, H., Zhao, T., Newland, B., et al. (2018). Catechol functionalized hyperbranched polymers as biomedical materials. *Prog Polym Sci,* 78, 47–55. **DOI.**org/10.1016/j.progpolymsci.2017.09.002
63. Johnston, W. T. (2008). The discovery of aniline and the origin of the term “aniline dye.” *Biotechnic and Histochemistry*, 83, 83–87. **DOI.**org/10.1080/10520290802136793
64. Rasmussen, S. C. (2017). The Early History of Polyaniline: Discovery and Origins. *Substantia*, *1*(2). **DOI.**org/10.13128/Substantia-30
65. Hofmann, A. W. (1843). Chemical investigation of organic bases in coal tar oil. *Ann Chem Pharm*, 47, 140.
66. Travis, A.S. (1994). From Manchester to Massachusetts via Mulhouse: The Transatlantic Voyage of Aniline Black. *Technology and Culture,* 35(1), 70-99. **DOI:**10.2307/3106749
67. Lightfoot, J. (1871). The Chemical History and Progress of Aniline Black. *Lower House, Lancashire.*
68. Noelting, E. (1889). Scientific and Industrial History of Aniline Black. *Wm. J. Matheson & Co., New York,* 1851-1922.
69. Travis, A. S. (1994). From Manchester to Massachusetts via Mulhouse: The Transatlantic Voyage of Aniline Black. *JSTOR*, 35(1), 70–99. **DOI.**10.1353/tech.1994.0118
70. Seymour, R.B. (1988). Polymers are everywhere. *J Chem Educ*, 65(4), 327-342.
71. H. Letheby (1862) XXIX. - On the production of a blue substance by the electrolysis of sulphate of aniline. *J Chem Soc*, 15, 161–163
72. Bibault, E. (1983). Les polymers conductrrs d’electricite: des “metaux syntetiques” riches en promesses. *Actualite chimique*, 7, 23–30.
73. Zollinger, H. (2004). Color Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments. third revised. *Wiley*, 43(40), 5291-5292. **DOI.**org/10.1002/anie.200385122
74. Kang, E., Neoha, K., G, Tanh, K. L. (1998). Polyaniline: A Polymer with Many Interesting Intrinsic Redox States. *Progress in Polymer Science*, 23(2), 277-324. **DOI.**org/10.1016/S0079-6700(97)00030-0
75. Palaniappan, S. (2008). Electrochemical co-polymerization of aniline and o-phenylenediamine. *J Solid State Electrochem,* 12, 953–962.
76. Wang, Z., Liao, F., Yang, S., Guo, T. (2012). Synthesis of poly (o-phenylenediamine)/ ferric oxide composites with rose-like hierarchical microstructures. *Mater Lett*, 67, 121–123. **DOI:**10.1016/j.matlet.2011.09.032
77. Samanta, S., Kar, P. (2015). Influence of pH of the reaction medium on the structure and property of conducting poly (o-phenylenediamine). *Mater Today Proc,* 2, 1301–1308. **DOI:**10.1016/j.matpr.2015.07.046
78. Kannapiran, N., Muthusamy, A., Anand, S., Jayaprakash, R. (2018). Synthesis, Structural, Magnetic and Electrical Characterization of Poly(o-phenylenediamine)/CoFe2O4 Nanocomposites. *J Supercond Nov Magn*, 31, 1489–1497. **DOI.**org/10.1007/s10948-017-4343-7
79. Zhang, X., Li, G., Wang, J., Chu, J., Wang, F., Hu, Z., Song, Z. (2022). Revisiting the Structure and Electrochemical Performance of Poly(o-Phenylenediamine) as an Organic Cathode Material. *ACS. Appl Mater Interfaces,* 14, 27968-27978. **DOI:**10.1021/acsami.2c06208
80. Ariffin, A. A., O’Neill, D. R., Yahya, M.Z.A., Zain, Z.M. (2012). Electropolymerization of ortho-Phenylenediamine and its Use for Detection on Hydrogen Peroxide and Ascorbic Acid by Electrochemical Impedance Spectroscopy. *International Journal of Electrochemistry*, 7, 10154–10163. **DOI:**10.1016/S1452-3981(23)16266-3
81. Li, X.-G., Huang, M.-R., Yang Y-L. (2001). Synthesis and characterization of o-phenylenediamine and xylidine copolymers. *Polymer (Guildf),* 42, 4099–4107. **DOI:**10.1016/S0032-3861(00)00661-3
82. Lan, H., Muslim, A., Hojiahmat, M., et al. (2021). Morphology formation mechanism and electrochemical performance of poly(o-phenylenediamine) based electrode materials. *Synth Met,* 273, 116688.

DOI.org/10.1016/j.synthmet.2020.116688

83. Bourezgui, A., Al-Hossainy, A.F., El Azab, I.H., et al. (2021). Combined experimental and TDDFT computations for the structural and optical properties for poly (ortho phenylene diamine) thin film with different surfactants. *Journal of Materials Science: Materials in Electronics*, 32, 5489–5503. **DOI.**org/10.1007/s10854-021-05271-4
84. Su, C., Ma, J., Han, B., Xu, L. (2021). Preparation of graphene oxide/poly(o-phenylenediamine) hybrid composite via facile in situ assembly and post-polymerization technology for the anode material of lithium ion battery. *Journal of Solid State Electrochemistry,* 25, 535–544. **DOI.**org/10.1007/s10008-020-04827-4
85. Sousa, M.S.P., de Sá, A.C., de Oliveira, J.P.J., et al. (2020). Impedimetric Sensor for Pentoses Based on Electrodeposited Carbon Nanotubes and Molecularly Imprinted poly-o-phenylenediamine. *ECS Journal of Solid State Science and Technology*, 9(4), 041006. **DOI.**org/10.1149/2162-8777/ab85bd
86. Cheng, Y., LYX; YLY; YSG (2023). Poly-(o-Phenylenediamine)-Decorated V4C3Tx Mxene/Poly(o-Phenylenediamine) Blends as Electrode Materials to Boost Storage Capacity for Supercapacitors and Lithium-Ion Batteries. Cheng, Y., LYX; YLY; YSG (2023). Poly-(o-Phenylenediamine)-Decorated V4C3Tx Mxene/Poly(o-Phenylenediamine) Blends as Electrode Materials to Boost Storage Capacity for Supercapacitors and Lithium-Ion Batteries. *ACS Appl Nano Mater,* 6, 9186–9196. **DOI.**org/10.1021/acsanm.3c00624
87. Deng, W., Zhang, Y., Tan, Y., Ma, M. (2017). Three-dimensional nitrogen-doped graphene derived from poly-o-phenylenediamine for high-performance supercapacitors. *Journal of Electroanalytical Chemistry,* 787:103–109. **DOI.**org/10.1016/j.jelechem.2017.01.047
88. Chen, C., Qiu, S., Qin, S., et al. (2017). Anticorrosion performance of epoxy coating containing reactive poly (o-phenylenediamine) nanoparticles. *Int J Electrochem Sci*, 12, 3417–3431. **DOI.**org/10.20964/2017.04.47
89. Rahman, N., Nasir, M. (2018). Application of Box–Behnken design and desirability function in the optimization of Cd(II) removal from aqueous solution using poly(o-phenylenediamine)/hydrous zirconium oxide composite: equilibrium modeling, kinetic and thermodynamic studies. *Environmental Science and Pollution Research*, 25, 26114–26134. **DOI.**org/10.1007/s11356-018-2566-1
90. Smiley, R.A. (2000). Phenylene- and Toluenediamines. In: Ullmann’s Encyclopedia of Industrial Chemistry. Wiley, **DOI.**org/10.1002/14356007.a19_405
91. Chan, .H.S.O., Ng, S.C., Hor, T.S.A., Sun, J., Tan,K.L., Tan, B.T.G. (1991). Poly(*m*-phenylenediamine): Synthesis and characterization by X-ray photoelectron spectroscopy. *European Polymer Journal,* 27(11), 1303-1308. **DOI.**org/10.1016/0014-3057(91)90069-Z
92. Kimura, Y., Tsucida A., Katsuraya, K. (2016). The Society of Fiber Science and Technology, Japan High-Performance and Specialty Fibers Concepts, Technology and Modern Applications of Man-Made Fibers for the Future. Springer, 1-451. ISBN 4431552030, 9784431552031.
93. Rebouillat, S., Steffenino, B. (2006). High performance fibres and the mechanical attributes of cut resistant structures made therewith. *In: WIT Transactions on the Built Environment. 86,* 279–299. **DOI:**10.2495/HPSM06028
94. Li, X.G., Huang, M. R., Duan, W., Yang, Y.L. (2002). Novel multifunctional polymers from aromatic diamines by oxidative polymerizations. *Chem Rev,* 102, 2925–3030. **DOI.**org/10.1021/cr010423z
95. Le, T. H., Kim, Y., Yoon, H. (2017). Electrical and electrochemical properties of conducting polymers. *Polymers, 9*(4), 150. **DOI.**org/10.3390/polym9040150
96. Ayankojo, A., Reut, G., Boroznjak, R., Öpik, A., Syritski, V. (2018). Sensors and Actuators B: Chemical Molecularly imprinted poly (meta-phenylenediamine) based QCM sensor for detecting Amoxicillin. *Sens Actuators B Chem,* 258, 766–774. **DOI:**10.1016/j.snb.2017.11.194
97. Amer I., Young, D.A., Vosloo, H.C.M. (2013). Chemical oxidative polymerization of m-phenylenediamine and its derivatives using aluminium triflate as a co-catalyst. *Eur. Polym. J,* 49, 3251–3260. **DOI.**org/10.1016/j.eurpolymj.2013.06.031
98. The colourful chemistry of artificial dyes. https://www.sciencehistory.org/education/scientific-biographies/william-henry-perkin/
99. Chatzi, E.G., Koenig, J.L. (1987). Morphology and Structure of Kevlar Fibers: A Review. *Polymer-Plastics Technology and Engineering*, *26*(3-4), 229-270.
100. Reashad, E., Kabir, B., Ferdous, E.N. (2012). Kevlar-The Super Tough Fiber. *International Journal of Textile Science,* 1(6), 78–83. **DOI.**org/10.5923/j.textile.20120106.04

101. Abdullayev, Y., Rzayev, R., Autschbach, J. (2022). Computational mechanistic studies on persulfate assisted p-phenylenediamine polymerization. *Journal of Computational chemistry Wiley Online Library, 43*,1313–1319. **DOI.**org/https://doi.org/10.1002/jcc.26943

102. Negi, A. (2025). Natural Dyes and Pigments: Sustainable Applications and Future Scope. *Sustain. Chem, 6*(3), 23. **DOI.**org/10.3390/suschem6030023

103. Meyer, A., Fischer, K. (2015). Oxidative transformation processes and products of para-phenylenediamine (PPD) and para-toluenediamine (PTD)—a review. *Environ Sci Eur,* 27(11). **DOI.**org/10.1186/s12302-015-0044-7

104. Xiong, S., Li, Z., Gong, M., et al. (2014). Covalently Bonded Polyaniline and para- phenylenediamine Functionalized Graphene Oxide: How the Conductive Two-dimensional Nanostructure Influences the Electrochromic Behaviors of Polyaniline. *Electrochim Acta. 138,* 101–108. **DOI.**org/10.1016/j.electacta.2014.06.108