Synthesis and Analysis of Multifunctional Nano-Scale Conductive (Co)-Oligomers Based on Meta-Phenylene Diamine and Pyrocatechol

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Abstract The oligomer was synthesized from the monomer m-phenylenediamine and pyrocatechol in an acidic medium under ultrasound, using potassium persulfate ($K_2S_2O_8$) as an oxidant. The structure and properties of synthesized oligomer were investigated by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), and NMR (^{13}C-NMR and ^{1}H-NMR) spectroscopies. The FTIR and NMR analysis revealed that oligomers contain amin (-NH) and hydroxyl (-OH) groups. An SEM examination of the synthesized material showed that its morphology **has a smooth surface.** The nanofibers are characterized by a length of several micrometers and a diameter in the range of 100–500 nm.

Keywords meta phenylenediamine, poly-(meta phenylenediamine), pyrocatechol (1,2-benzenediol)

I. Introduction

Over the last two decades, polyconjugated aromatic diamine polymers have received significant attention in polymer research due to their extraordinary properties, such as versatility, easy processability, good thermal stability, architecture flexibility, multi-functionality, good electroactivity, variable conductivity, colorful electrochromic feature, good mechanical and optical properties, environmental stability, magnetic activity, lightweight, and low-cost production. These polymers have been investigated in the application of supercapacitors, electrode materials, batteries, LED, OLED, antistatic coating, corrosion inhibitors, electronics, electrochromic devices, electrocatalysis, etc.

Although phenylenediamines belong to aniline derivatives, poly-phenylenediamines display different properties than polyaniline. Phenylenediamine can be synthesized via chemical and electrochemical methods.

P-phenylenediamine (PPD) is a derivative of aromatic amine and is widely used in organic and coordination chemistry [1]. The first application of PPD to generate an azo dye in 1863 opened a new area in the synthesis of organic dyes [2] . Nowadays, PPD is still used as an intermediate for producing technical azo dyes and printing inks [3, 4].

Moreover, it is also used as an effective adsorption material [5], a precursor to specific polymers, plastics, and fibers, as a photographic developing agent, and as a histological stain for some lipidsysical [6, 7].

Polymers derived from ortho-phenylenediamines (OPD) are known for their unique physicochemical properties, primarily attributed to their molecular structure's pyrazine and phenazine rings [8]. These heterocyclic moieties significantly enhance the resulting materials' thermal stability, chemical resistance, and electrochemical activity [9, 10]

Poly-(m-phenylenediamine) was prepared by oxidizing m-phenylenediamine in an acidic aqueous solution [11–14], concentrated hydrochloric acid [60], or water.

Meta-phenylenediamine (mPD) is a highly versatile aromatic diamine that is a key precursor in synthesizing various high-performance polymers and industrial materials. It is crucial in producing aramid fibers, epoxy resins, wire enamel coatings, polyurea elastomers, and adhesive resins. It also finds extensive use in dye formulations for leather, textiles, and hair color products.

Pyrocatechol (1,2-benzenediol), a phenol derivative, is primarily utilized in pesticide manufacturing. It also serves as an essential intermediate in synthesizing fine chemicals, including fragrances and pharmaceutical compounds.

Problem Statement

Although extensive research has been conducted on polyaniline and other aniline-based conductive polymers, there is an increasing demand for alternative monomers and copolymers with customizable properties. These include improved solubility, thermal stability, and mechanical strength while maintaining adequate conductivity. Meta-phenylenediamine and pyrocatechol stand out due to their aromatic structures and functional groups, making them promising candidates for polymer development. However, optimizing the polymerization process to achieve a well-balanced combination of conductivity and structural integrity remains challenging. This study aims to bridge this gap by synthesizing and analyzing a polyfunctional nano-sized copolymer derived from meta-phenylenediamine and pyrocatechol.

Chemical preparation of poly (m-phenylenediamine-co-pyrocatechol) oligomer: In a 500 mL three-neck round-bottom flask equipped with an ultrasonic homogenizer and reflux condenser, OPD, pyrocatechol, and 100 mL of 1M HCl were introduced. A separate oxidant solution was prepared by dissolving potassium persulfate (PPS) in 40 mL of deionized water. Once the reaction commenced, the oxidant solution was gradually added dropwise over 30 to 40 minutes. The reaction was conducted under an argon (N_2) atmosphere, maintained at 80 °C, and stirred continuously for six hours. Upon completion, the reaction mixture was allowed to cool to room temperature and then filtered. The resulting solid was thoroughly washed with water and methanol several times before being dried under a vacuum (13.3 Pa) at 60 °C for 48 hours to facilitate characterization. This process yielded a fine black powder with a 70 % recovery. The synthesized compounds exhibited good solubility in polar organic solvents such as DMSO, DMF, and acetone.

The synthesized material's composition, structure, and features were determined by elemental, chemical, and spectral analysis methods (FTIR, NMR, and SEM).

The Fourier-transform infrared (FTIR) spectrum revealed characteristic absorption bands corresponding to key functional groups in the synthesized polymer. The N–H bond stretching vibrations associated with aromatic amines were detected at 3226 cm^{-1}. Additionally, distinct peaks within the benzene ring appeared around 1570 cm^{-1}, attributed to the stretching vibrations of benzenoid (C=C) structures. The absorption bands at approximately 1491 cm^{-1} were linked to stretching the phenol group's C–O–H bond, a feature absent in poly-paraphenylenediamine. Further analysis identified absorption bands at 1288 cm^{-1} and 1339 cm^{-1}, corresponding to the stretching vibrations of C–O and C–N bonds within the amine groups, respectively. Moreover, the bands observed at 685 cm^{-1}, 782 cm^{-1}, and 830 cm^{-1} were associated with the out-of-plane deformation of C–H bonds in the aromatic ring, confirming the presence of aromatic structures in the polymer.

NMR spectra confirmed the structure of oligomers. The chemical shift for aromatic hydrogens appeared at 6,7 δ (multiplet) and 7,2 δ (multiplet) in the ^{1}H-NMR spectrum of the synthesized oligomer. In addition, a strong pick was observed at 5,8 δ can be attributed to the aromatic hydroxyl group. The chemical shifts of aromatic carbon atoms in the oligomer were observed in the ^{13}C-NMR at 147 ppm, 139 ppm, 130 ppm, 113 ppm, 110 ppm, and 96 ppm [10].

Scanning electron microscopy (SEM) was used to study the surface morphology and internal structure of synthesized oligomers. The co- oligomer's morphology has a smooth surface, and the particles are nanoscale.

Conclusion

The poly-(mPD-co-1,2-pyrocatechol) nanocomposite was synthesized via the oxidative polycondensation method. Oligomes were characterized using FTIR and NMR spectroscopy.

FTIR, ^{13}C NMR, and ^{1}H NMR analyses confirmed the oligomer contains amine and hydroxyl functional groups. Additionally, SEM analysis confirmed that the oligomer consisted of nanoparticles and had a smooth surface.

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