

Scientific paper

Synthesis and Characterization of Nano-Sized Poly(1,4-Diaminonaphthalene) in Potassium Persulfate

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Abstract

A novel poly(1,4-diaminonaphthalene) was synthesized from the monomer 1,4-diaminonaphthalene at the nanoscale via an oxidative polymerization method. The reaction was conducted in an acidic (HCl) medium under an ultrasound homogenizer at 0 °C, while potassium persulfate was used as a radical initiator. This polymer has been characterized using various techniques, including FTIR, UV-Vis spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), NMR analysis, and electron paramagnetic resonance (EPR) methods. The nanopolymers were found to be thermally stable up to 200 °C. EPR data further substantiated the presence of unpaired electrons on the nitrogen atoms within the polymer backbone.

Keywords: Conductive polymers, 1,4-diaminonaphthalene, poly(1,4-diaminonaphthalene), semiconductor, oxidative polymerization

1. Introduction

Due to their high resistance properties, organic polymers had limited applications as insulators in electrical settings until the discovery of conducting polymers.^{1–3} Conductive organic polymers are a class of synthetic polymers that have poly-conjugated chains with alternating single and double bonds,^{4–6} which allows the delocalization of electrons along the polymer chain.^{7–9} The charge mobility within the polymers leads to their electrical conductivity.^{10,11} Since the discovery of conductive polymers, polymers of aromatic amines,^{12–14} especially polyaniline (PANI) and its derivatives (diamine benzene, toluidine, etc.),^{15–17} have attracted remarkable attention due to their outstanding chemical,^{18,19} and physical properties.^{20–22}

These polymers have various applications and properties, such as electrical conduction, optical,²³ and magnetic properties,^{24,25} charge transfer, and electromagnetic shielding,^{26,27} due to conjugated π bonds. These attributes have led to their utilization in various fields, such as anti-static coating,^{28–30} corrosion material,^{31–35} electrochromic glass,^{36,37} supercapacitors,^{38,39} flexible electrodes,^{39–41} light emitting devices,⁶ sensors,^{42–45} conductive fibers,^{46–48} solar cell fabrication,⁴⁹ transducers, plastic batteries,^{50–52} and so on. Despite many superior properties, a major limitation of PANI is its low thermal stability, poor processability, and extremely poor solubility in common organic solvents.^{53–55}

Ongoing research aims to address current challenges and develop new polymers with enhanced environ-

mental and thermal stability. Although poly(naphthylamine) (PNA) and PANI belong to the same family of polyaromatic amines, their chemical and physical properties are different due to their polymer backbone. In contrast to aniline and its derivatives, aminonaphthalenes have only recently drawn interest as conductive polymers, despite their significant potential to address key challenges.

In 1981, the electrochemical polymerization of 1-naphthylamine (1-NA) was reported by Vettorazzi and another research team.^{56,57} Subsequently, Arévalo *et al.* carried out the electrooxidation of 1-naphthylamine (ArNH_2) in aqueous acid media.⁵⁸ Later, in 1993, Moon *et al.* reported the chemical polymerization of 1-NA using H_2O_2 and Fe as catalysts.⁵⁹ It was found that this polymer exhibited relatively high electrical conductivity.⁶⁰ In this context, Shaffie synthesized conductive poly(1-NA) by chemical oxidative polymerization methods.⁶¹ Shan conducted a study demonstrating synthesis of poly(1-NA) via enzymatic polymerization.⁶² As a derivative of PANI, PNA shares numerous benefits, such as facile synthesis, adjustable redox characteristics, pH-responsive electrochromic properties, and easy doping-dedoping capabilities.^{63,64} One notable drawback of PANI lies in its limited thermal stability and challenging processability, which can be enhanced by introducing substituents onto the ring structure.^{65,66}

Poly(1-naphthylamine) may exhibit higher electrochemical activity because of its larger conjugated system and stronger electron delocalization. Therefore, it has a wide range of applications, such as LEDs,^{63,67} electro-catalysis,⁶⁸ sensors,⁶⁹ anti-corrosion,^{70–72} antibacterial activity,⁷³ porous polymer.^{63,74} Good thermal stability, improved crystallinity, enhanced solution processability in common organic solvents, and promising potential applications make PNA an excellent alternative to PANI.^{75,76}

Diaminonaphthalene (DAN) is a naphthalene derivative formed by attaching an $-\text{NH}_2$ group at various positions on the second condensed benzene ring of the molecule.⁷⁷ Over the past thirty years, several studies have been conducted on the synthesis and characterization of poly(diaminonaphthylene) (PDAN), along with its copolymers and nanocomposites.^{78–81}

An extensive review of the literature reveals that while numerous DAN derivatives have been examined, some remain inadequately studied. In particular, the polymerization mechanism of the 1,4-DAN monomer and the resulting physical, mechanical, and chemical properties of the resulting polymer have not been thoroughly investigated. Therefore, researching the polymerization of 1,4-DAN, assessing its properties, and exploring its potential applications are essential for advancing our understanding in this field.

The aim of this study was the synthesis of nanoscale poly(1,4-diaminonaphthylene) using the chemical oxidative-polycondensation method.

2. Materials and Methods

2. 1. General Information

1,4-Diaminonaphthalene (1,4-DAN, 98 wt%), dodecylamine (DDA, 98 wt%), potassium persulfate (PPS, $\text{K}_2\text{S}_2\text{O}_8$, ≥ 99.0 wt%), methanol (CH_3OH , ≥ 99.9 wt%), hydrochloric acid (HCl, 37 vol%), and all other solvents were purchased from Sigma Aldrich (Germany). All chemicals used were of analytical grade and used as received without any further purification. Removal of all solvents was carried out under reduced pressure. Deionized water was used throughout all the experimental processes.

2. 2. Characterization

The molecular structure of nanocomposites was characterized by an FT-IR (Bruker Alpha-P in ATR in the range of $400\text{--}4000\text{ cm}^{-1}$, Wismar, Germany) spectrometer. The solution of polymers in dimethyl sulfoxide (DMSO) were used for recording UV-visible absorption spectra (Shimadzu UV-2600, Japan). The thermal stability of the polymer was investigated by thermogravimetric analysis (TGA), which was performed on an STA 6000 model (Perkin Elmer Instruments, USA) under nitrogen flow ($20\text{ cm}^3\text{min}^{-1}$) within the temperature interval from $25\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{Cmin}^{-1}$. The XRD was measured with Bruker AXS D8 Advance (Wismar, Germany). The samples were mounted on conductive carbon tape and coated with a 20 nm layer using direct current sputtering. To analyze the morphology of the nanocomposites, scanning electron microscopy (SEM) images were taken by field emission JEOL SEM 7001F (Tokyo, JAPAN) acquired in secondary electron imaging (SEI) mode.

Ultrasonic homogenizers and ultrasonic emulsification device probe sonicators (FS3N140303, 100 w, 40 Hs, manufactured in the USA) have been used in polymer synthesis to enhance the reaction rate through cavitation produced by ultrasonic energy. This cavitation leads to the formation and collapse of tiny bubbles, giving rise to solubility, diffusivity, penetration, and transportation of monomers in the media.

^1H NMR spectra were recorded for 2% solutions on a Bruker-Ultrashield (400 MHz) (Bruker, MA, USA). The ^1H NMR spectra were calibrated using the $\text{DMF-}d_7$ solvent peak at 2.93 ppm. Chemical shifts (δ) are given in parts per million (ppm), referring to the signal center using the deuterated solvent peaks as reference.

Samples containing free radicals A (1) in the polycrystalline state were studied by electron paramagnetic resonance (EPR) at room temperature using a SE/X-2544 EPR spectrometer. The microwave frequency used was 9.4 GHz.

Synthesis of poly(1,4-diaminonaphthalene) nanoparticles. Poly-1,4-DAN nanoparticles were obtained by chemically oxidative polymerization of 1,4-DAN in hydrochloric (HCl) aqueous solution using potassium per-

sulfate (PPS, $K_2S_2O_8$) as an oxidant. Dodecylamine (DDA) has been used as a surfactant to synthesize nanosized conductive polymers.

The ultrasonication technique was employed in this synthesis to generate and collapse microscopic bubbles, enhancing the solubility, diffusivity, penetration, and transportation of monomers within the medium. The technique offers high reaction rates, homogeneous chain growth, and higher yields and operates under mild conditions. As a typical procedure, in this experiment, 1,4-DAN (25 mmol, 3.95 g) and DDA (2.1 mmol, 0.4 g) were added into a 500 mL three-neck round-bottom flask equipped with an ultrasonic homogenizer and reflux condenser. In addition, HCl (150 mL, 1 M) was added to the flask to prepare the 1,4-DAN salt. Furthermore, the mixture was pre-cooled and stirred constantly in an ice bath to make a homogenous solution. The oxidant solution was prepared by dissolving PPS (12.5 mmol, 3.375 g) in deionized water (50 mL). Subsequently, the oxidant solution was added to the reaction mixture in the ratio of monomer:oxidant (2:1 w/w) drop by drop to the monomer solution for 30 min to initiate the polymerization process. The flask was subjected to sonication for 3 hours at 0 °C, and was kept in a deep freezer for 24 hours. The product was collected by filtra-

tion and washed completely with deionized water to remove impurities such as unreacted monomers, inorganic salts, oxidants, and HCl. It was then washed with methanol, filtered, and dried under a vacuum at 60 °C for 24 hour.

The product was treated with an ammonia solution (1.5 M, deprotonation), washed with a concentrated sulfuric acid solution (6 M, re-protonation), and stirred for 3 hours. Finally, the resulting product was filtered and dried again under vacuum.

The purified poly-1,4-DAN has been characterized using various techniques such as spectroscopy (UV-Vis, IR, NMR), morphology (SEM), thermal analysis (TGA), and EPR measurements.

3. Results and Discussion

FT-IR analysis. To more accurately talk about the structure of the resulting polymer, the polymerization reaction of 1,4-DAN was carried out without the presence of a surfactant in the reaction mass while maintaining the remaining conditions for the polymerization reaction as when obtaining the corresponding nano-sized polymer.

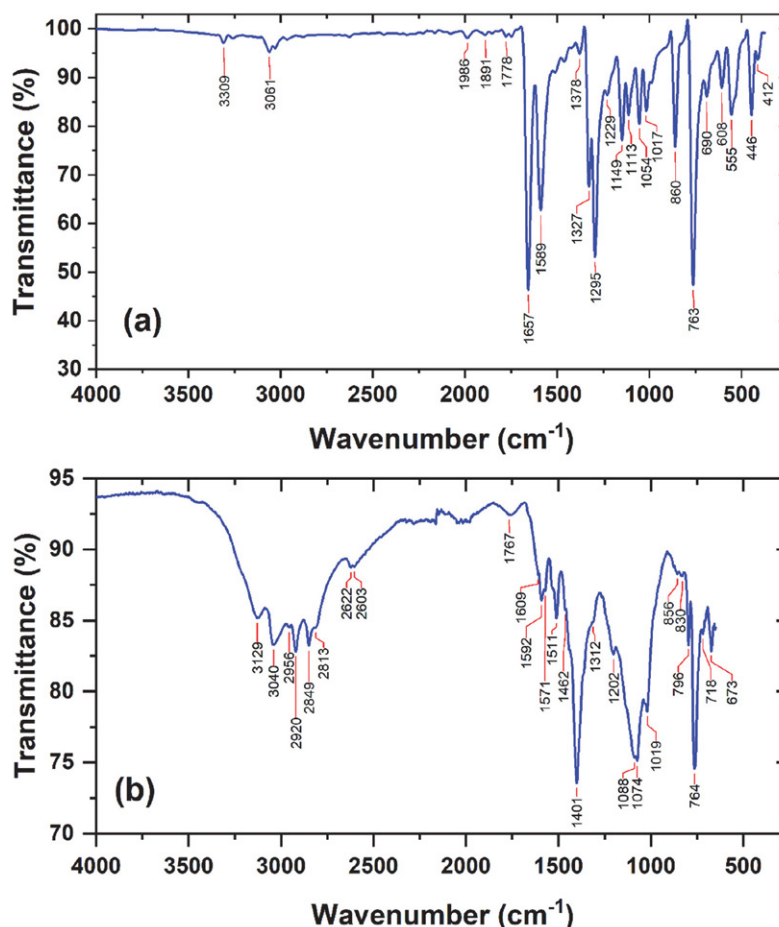


Figure 1. FT-IR absorption spectrum of 1,4-PDAN in potassium persulfate ($K_2S_2O_8$): (a) without surfactant; (b) with surfactant.

The IR spectrum for such poly-1,4-DAN is shown in Figure 1a. The relatively sharp peak at 3060 cm^{-1} can be attributed to the aromatic C–H out-of-plane bending vibration. The two bands at 1657 cm^{-1} and 1589 cm^{-1} are ascribed to the C=C stretching vibration of naphthalene rings of the polymer skeleton. It should be noted that there are no signals that could correspond to the N–H stretching vibrations of the amine group, which may indicate that polymerization under these conditions proceeds in such a way that no secondary amine is formed; most likely, a corresponding imine is formed in resulting poly-1,4-DAN. Characteristic peaks at $1378\text{--}1295\text{ cm}^{-1}$ indicate the presence of C–N–C stretching vibrations and may reflect the quinoid and benzenoid structures in the polymer backbones. The strong signal at 763 cm^{-1} is characteristic of aromatic out-of-plane C–H bending vibrations.

In contrast to the previous case, in Figure 1b is presented the polymer obtained in the presence of surfactant. Along with the peaks characteristic for poly-1,4-DAN, the spectrum also includes peaks associated with aliphatic amines, namely DDA. So we can observe the presence of peaks at 3129 cm^{-1} that correspond to the stretching absorption of N–H bonds, in the $2956\text{--}2813\text{ cm}^{-1}$ region characteristic for asymmetric and symmetric sp^3 C–H stretching vibrations, and in the $1401\text{--}1312\text{ cm}^{-1}$ region which belong to the scissoring C–H vibrations and methyl rock vibrations, as well as strong and wide peaks in the $1088\text{--}1019\text{ cm}^{-1}$ region characteristic for the aliphatic stretch C–N vibrations of the amino group.

By comparing both spectra, it is evident that the final product contains a significant amount of sulfate in the sample, which is a consequence of the nanosize of the resulting particles, which have a large surface area and, as a result, a significant amount of DDA was required to envelop them.

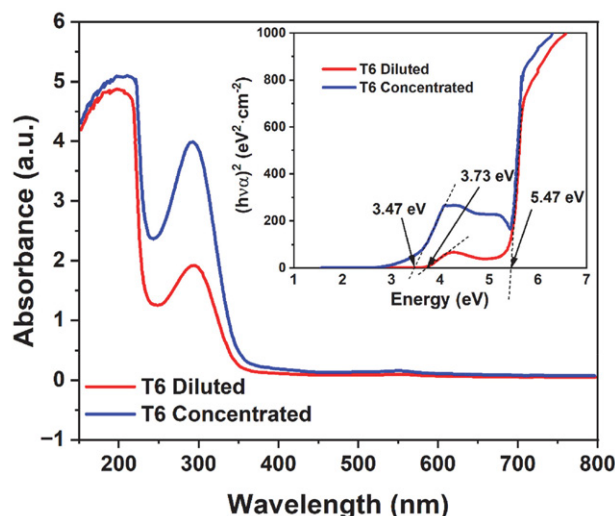


Figure 2. The UV-Vis spectra of poly-1,4-DAN. Inset: the Tauc plot of poly-1,4-DAN, illustrating the relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$). [Note: blue and red color belong to concentrated and diluted DMSO solution, respectively].

UV-Vis analysis. The UV-Vis spectra of poly-1,4-DAN polymers were measured in DMSO (Figure 2). The synthesized polymer's UV-Vis spectra showed two strong absorption bands at 250 and 345 nm. The absorption band at around 250 nm was ascribed to the p^*p^* transition associated with the --N= functional groups of the polymers, and the second absorption band in the region 345 nm was assigned to the n^*p^* transitions in quinoid units of the long conjugated polymer chain. Although the shapes of the spectra are identical, the intensity of the peaks decreases in the diluted sample. In the Tauc plot of poly-1,4-DAN polymers, two distinct linear regions are observed as can be seen from the inset in Figure 2. For the concentrated and diluted samples, optical band gap values of 3.47 eV and 3.73 eV, respectively, are obtained, while the higher band gap of 5.47 eV is the same for both samples.

Thermogravimetric analysis. The thermal degradation of poly-1,4-DAN was studied using thermogravimetric methods. TG analysis data show that the decomposition of the polymer proceeds in two steps, as is illustrated in corresponding curve shown in Figure 3. In the TGA, the first significant weight loss in the interval $105\text{--}200\text{ }^\circ\text{C}$ is due to the loss of up to 85% which can be attributed to the thermal degradation of the copolymer backbone,⁸² while derivative thermogravimetric analysis (DTGA) indicated a pronounced peak at $180\text{ }^\circ\text{C}$, suggesting a maximum rate of decomposition at this temperature. Further, starting from $200\text{ }^\circ\text{C}$ up to $750\text{ }^\circ\text{C}$, the TGA curve showed a gradual and continuous weight loss with a small slope, indicate that the copolymer undergoes near-complete decomposition, resulting in the formation of low molecular mass particles, with only 5.31% of the weight remaining. This suggest a relatively high thermal stability of the polymer remaining after the initial decomposition.

NMR spectrum In the ^1H NMR spectrum, signals are observed in the low field at 9.5–7.0 ppm, corresponding to the chemical shift of the aromatic protons of the

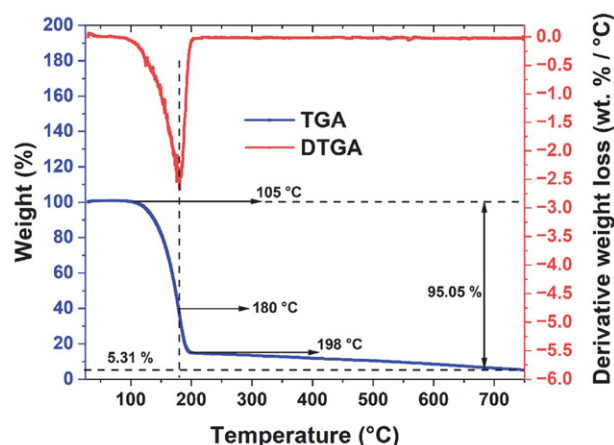


Figure 3. TGA (blue) and DTGA (red) curves of the polymer powders of poly-1,4-DAN at heating up to $750\text{ }^\circ\text{C}$ with a rates of $10\text{ }^\circ\text{C} \times \text{min}^{-1}$.

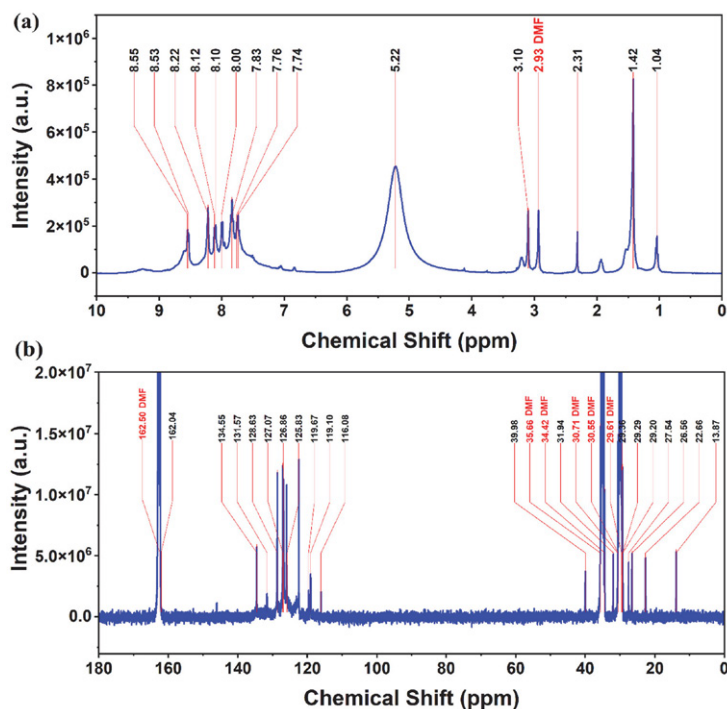
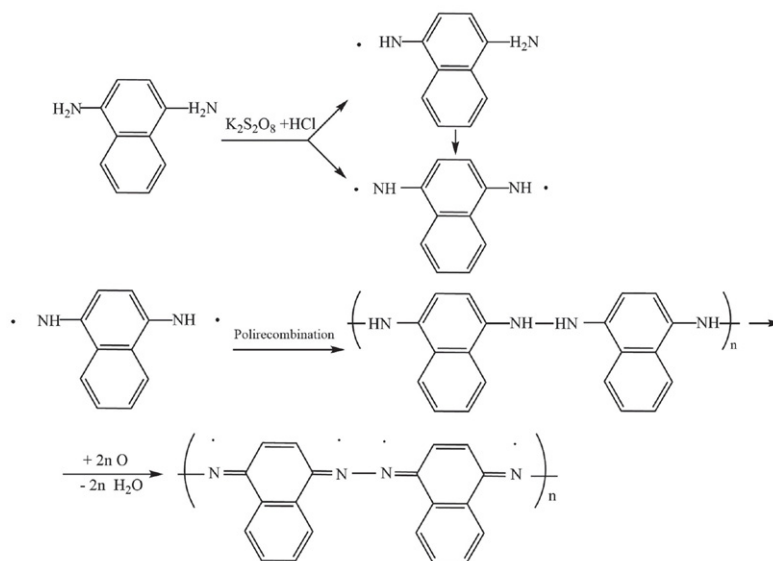


Figure 4. The (a) ¹H NMR and (b) ¹³C NMR spectrum of poly-1,4-DAN in DMF-*d*₇.

naphthalene ring overlapping with proton signals of the NH₂ group of DDA (Figure 4a). The shape and number of peaks confirm the polymeric structure of the sample. Signals in the high field at 1.04 and 1.42 ppm, characteristic of aliphatic fragments of DDA, are also present in the ¹H NMR spectrum. Analysis of the ¹³C NMR spectra also confirms the presence of signals in the high field (see Figure 4b), attributed to the presence of a sufficient amount of surfactant in the samples, necessary for the formation of

nanoparticles. The signals in the low field in the ¹³C NMR spectrum the same confirm the presence of aromatic carbons in the sample (see Scheme 1).

Scanning Electron Microscopy. SEM images provide a complex detail of the morphology of the synthesized material 1,4-diaminonaphthalene as a monomer, K₂S₂O₈ as oxidant, and dodecylamine as a surfactant at 0 °C. On the surface of the synthesized sample, pronounced agglomerations of particles are observed, forming blocks



Scheme 1. Proposed scheme of polymerization of 1,4-DAN in acidic medium.

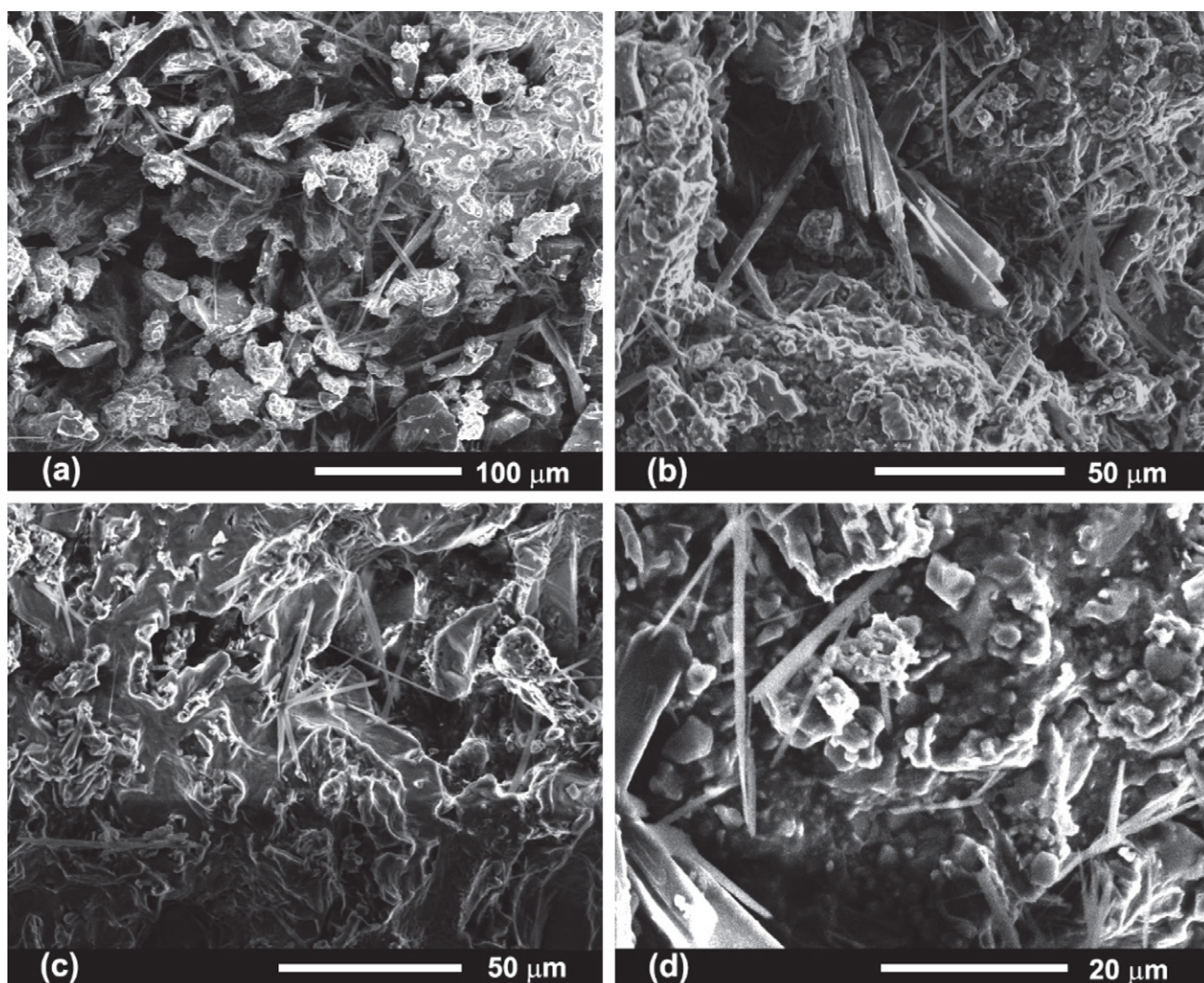


Figure 5. SEM images at different magnifications of poly-(1,4-DAN) nanoparticles synthesized by chemical oxidation.

with variable sizes between 10–50 μm . On a larger scale investigation, it is observed that these blocks are often composed of conglomerates of smaller particles with dimensions below 1 μm . This behavior can be explained by particle adhesion and coalescence processes during synthesis under the influence of local conditions and the surfactant used. Near the large clusters, elongated thread-like structures with lengths of approximately 25 μm and diameters between 1–2 μm are also observed. The use of ultrasound during the synthesis is anticipated to have a significant impact on material morphology. It was expected that ultrasonic energy would facilitate the uniform dispersion of reagents in solution and influence the formation of particles of controlled sizes, depending on the operating parameters and duration of exposure. However, the observed particle sizes vary significantly, indicating nonuniform growth and a large diversity of sizes and shapes, suggesting a highly complex synthesis process.

EPR analysis. It is known that the stable aromatic free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) is one

of the first and most widely used standard samples for determination of the g -factors of the spin species and for measuring the unpaired spin concentration using electron paramagnetic resonance (EPR).⁸³ It was found that the EPR spectrum of the poly-1,4-DAN measured in X-band at room temperature consists of a single line with g -factor $g = 2.0039 \pm 0.0006$ and peak-to-peak width $\Delta B_{\text{pp}} = (1.1 \pm 0.008)$ mT. The g -factor for poly-1,4-DAN is near to the g -factor for DPPH, which is used as a standard magnetic field marker $g = 2.0036 \pm 0.0002$.⁸³ The peak-to-peak EPR line width of poly-1,4-DAN is greater than ΔB_{pp} of DPPH. This indicates that in synthesized polymer, the exchange interaction between almost free electrons is weaker than in DPPH.

Polymerization mechanism of 1,4-DAN. Thus, based on the results of chemical and spectral analyses and relevant data available in the scientific literature,^{15,16} the following mechanism can be proposed for the oligomerization process of 1,4-diaminonaphthalene during oxidation in the presence of $\text{K}_2\text{S}_2\text{O}_8$:

As a result of the oxidation of 1,4-diaminonaphthalene with $K_2S_2O_8$ in an acidic environment, biradicals of diaminonaphthalene are formed. These biradicals undergo polyrecombination, resulting in oligomeric macromolecules composed of 1,4-diaminonaphthalene units, which then form oligomeric products with a naphthoquinone-imine structure in a strongly oxidizing environment.

4. Conclusions

As a result of the investigations carried out, the FT-IR spectrum of poly(1,4-diaminonaphthalene) displays bands at 3060 cm^{-1} and 3129 cm^{-1} , which can be attributed to aromatic C–H out-of-plane bending vibration and the stretching absorption of N–H bonds, respectively. The two bands at 1657 cm^{-1} and 1589 cm^{-1} are ascribed to the C=C stretching vibration of naphthalene rings of the polymer skeleton. The UV-Vis studies showed differences in the polymers' chain conformation and polaronic states. The UV-Vis showed strong absorption bands at 250 and 345 nm, related to p^*p^* and n^*p^* transitions, respectively.

Poly-1,4-DAN exhibits good thermal stability, allowing it to withstand high temperatures without significant degradation. This stability is beneficial for applications involving elevated temperatures or requiring long-term durability. The synthesized polymer also demonstrates good mechanical properties, including flexibility and strength. These characteristics enable its use in various flexible electronics, coatings, and films. The chemical structure of poly-1,4-DAN consists of repeating units of 1,4-diaminonaphthalene, resulting in a linear polymer chain. The presence of amino groups on the naphthalene ring allows for potential chemical modifications and functionalization, expanding its range of applications.

Altogether, the synthesis and characteristics of poly-1,4-DAN make it a promising material for electronic, optoelectronic, and other related applications, benefiting from its electrical conductivity, thermal stability, and mechanical properties.

Conflicts of Interest

The authors declare no conflicts of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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Povzetek

A novel poly(1,4-diaminonaphthalene) was synthesized from the monomer 1,4-diaminonaphthalene at the nanoscale via an oxidative polymerization method. The reaction was conducted in an acidic (HCl) medium under an ultrasound homogenizer at 0 °C, while potassium persulfate was used as a radical initiator. This polymer has been characterized using various techniques, including FTIR, UV-Vis spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), NMR analysis, and electron paramagnetic resonance (EPR) methods. The nanopolymers were found to be thermally stable up to 200 °C. EPR data further substantiated the presence of unpaired electrons on the nitrogen atoms within the polymer backbone.



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