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SINTEZA ȘI CARACTERIZAREA OLIGO-(*m*-FENILENDIAMINĂ-CO-1,3-BENZENDIOLULUI) PENTRU MATERIALE FUNCȚIONALE AVANSATE

Ramil RZAYEV[1], Natalia SUCMAN[1], Mammadov BAKHTİYAR[2], Fliur MACAEV[1]

[1]Institutul de Chimie al Universității de Stat din Moldova, [2]Institute of Polymer Materials, Azerbaijan National Academy of Sciences, Azerbaijan Republic

Rezumat

Metoda de policondensare oxidativă a fost utilizată pentru a sintetiza un oligomer pe bază de meta-fenilendiamină și rezorcinol, într-un mediu acid, utilizând persulfat de potasiu ca agent oxidant. Scopul acestui studiu a fost obținerea de materiale multifuncționale cu caracteristici fizico-chimice și calități electroactive îmbunătățite. Spectroscopia FTIR, RMN, ESR, analiza termogravimetrică (TGA) și microscopia electronică cu scanare (SEM) au fost utilizate pentru a caracteriza materialele sintetizate. Formarea scheletului polimeric și adăugarea de grupări amină și fenolice au fost verificate prin datele FTIR și RMN. Electronii nepereche au fost găsiți prin analiza ESR, sugerând un comportament electroactiv. În timp ce imaginile SEM au relevat o morfologie relativ uniformă, TGA a prezentat o bună stabilitate termică. Materialele obținute sunt promițătoare pentru utilizarea în sisteme și senzori electrochimici.

Cuvinte-cheie: Meta-fenilendiamină, 1,3-benzendiol (rezorcinol), persulfat de potasiu, polimerizare oxidativă.

SYNTHESIS AND CHARACTERIZATION OF OLIGO-(*m*-PHENYLENEDIAMINE-CO-1,3-BENZENEDIOL) FOR ADVANCED FUNCTIONAL MATERIALS

Abstract

The oxidative polycondensation method was used to synthesize an oligomer based on metha-phenylenediamine and resorcinol, in an acidic medium, utilizing potassium persulfate as an oxidizing agent. The goal of this study was to obtain multifunctional materials with enhanced physicochemical features and electroactive qualities. FTIR, NMR, ESR spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) were used to characterize the synthesized materials. The formation of the polymer backbone and the addition of amine and phenolic groups were verified by FTIR and NMR data. Unpaired electrons were found by ESR analysis, suggesting electroactive behavior. While SEM images revealed a comparatively uniform morphology, TGA showed good thermal stability. The materials that were obtained show promise for use in electrochemical systems and sensors.

Keywords: Metha-phenylenediamine, 1,3-benzenediol (resorcinol), potassium persulfate, oxidative polymerization.

Introduction

Because of their numerous applications in sensors, electronics, energy storage, and biomedical devices, the development of advanced functional materials based on conducting and semiconducting polymers has attracted significant attention. Among these materials, aromatic amine- and phenol-based polymers are especially interesting due to their adjustable physicochemical properties and structural flexibility [1–5].

The m-Phenylenediamine (m-PD) is a member of the aromatic diamines, commonly used as a monomer for the synthesis of electroactive oligomers and polymers. The m-PD shows lower conjugation than para-substituted analogues, resulting in unique electronic features and increased chemical stability. Oxidative polymerization of m-PD usually yields ladder-like and phenazine-type structures, which are well-suited for sensing and electrochemical applications [6].

Resorcinol (1,3-benzenediol), a dihydroxy benzene derivative, is an important building block in polymer chemistry. Strong hydroxyl groups that donate electrons make it more reactive in oxidative coupling and electrophilic substitution reactions. Resorcinol is widely used in the production of phenolic resins, carbon materials, and functional coatings, where it enhances crosslinking and structural diversity [7, 8].

Polyfunctional, versatile polymers with desired properties can be effectively obtained by using aromatic amines and phenols as starting monomers [9, 10]. An efficient method for creating multifunctional co-oligomers that integrate hydroxyl and amino functionalities into a single framework is the co-polymerization of m-PD and resorcinol. These hybrid materials may have better physicochemical characteristics, such as increased interaction with analyte molecules, tunable electrical conductivity, and improved solubility. Through radical-mediated C–C, C–N, and C–O bond formation, oxidative copolymerization with oxidants like potassium persulfate can create complex structures in acidic environments. This study carried out controlled oxidative polymerization to create oligo-(m-phenylenediamine-co-resorcinol). This work intends to explore the synthesis, structural features, and potential functional properties of the resulting co-oligomer, with the goal of its application in advanced material systems.

Materials and methods

The molecular structure of nanocomposites was characterized using a Fourier-transform infrared (FTIR) spectrometer (Bruker Alpha-P, ATR, 400–4000 cm-1, Wismar, Germany). Liquid NMR spectra (^{1}H-, ^{13}C-, ^{13}C^{1}H-HSQC, ^{13}C^{1}H-HMBC, ^{15}N^{1}H-HSQC, ^{15}N^{1}H-HMBC experiments) were recorded for 2% solutions in DMSO-d_6 at 400 MHz on either a Bruker-Avance III (Bruker, Rheinstteten, Germany), or a Bruker Avance Neo (Bruker, Ettlingen, Germany), Chemical shifts (δ) are given in parts per million (ppm), referring to the signal center using the deuterated solvent peaks as reference. For solid-state NMR, samples were recorded on a 400 MHz Bruker Avance Neo (Bruker, Ettlingen, Germany) using a 4 mm CP-MAS multinuclear probe. Samples have been spined at 10 KHz.

The thermal stability of the polymer was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), performed on a STA 6000 (Perkin Elmer Instruments, USA) under a nitrogen flow (20 cm³min-1) over the temperature range from 25 °C to 800 °C at a heating rate of 10 °C min-1. 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 obtained using a Field Emission JEOL SEM 7001F (Tokyo, Japan) in secondary electron imaging (SEI) mode. Samples containing free radicals A (1) in the polycrystalline state were studied by electron spin resonance (ESR) at room temperature using a SE/X-2544 EPR spectrometer.

Results and discussion

FT-IR, NMR, ESR, and SEM analyses were used to assess the structural and morphological characteristics of the synthesized material. The FTIR spectrum (Fig. 1) showed the characteristic absorption bands at 3675 and 3195 cm^{-1} assigned to free O–H stretching vibrations of phenolic groups (resorcinol units) and N–H stretching vibrations of aromatic amine groups (m-phenylenediamine), respectively. The peaks at 2988 and 2901 cm^{-1} are attributed to C–H stretching vibrations of aromatic and aliphatic fragments, indicating the presence of benzene ring structures. The bands at 1614 and 1450 cm^{-1} are attributed to benzenoid (C=C) and quinoid (C=N) stretching, respectively, while the signals at 1394 and 1383 cm^{-1} are associated with C–N stretching vibrations of aromatic amine groups and possible contributions from phenolic O–H bending. Furthermore, 1250 and 1230 cm^{-1} characteristic of C–N stretching (aromatic amine) and C–O stretching (phenolic groups), indicating successful incorporation of both monomer

units into the oligomer structure. Additionally, the bands at 843, 765, and 692 cm^{-1} are assigned to out-of-plane C–H deformation vibrations of isolated aromatic C–H groups and adjacent C–H groups, respectively. The oligomer structure was further examined by NMR spectroscopy. In the ^{1}H NMR spectrum, signals at 9.14, 7-7,5 and 5.56 ppm were observed. The signal at 5.56 ppm, together with a cross-peak at 94.8 ppm in the $^{1}H–^{13}C$ HSQC spectrum, confirms the presence of the resorcinol fragment. The signal at 9.14 ppm is attributed to the NH group of a *m*-phenylenediamine unit linked to resorcinol.

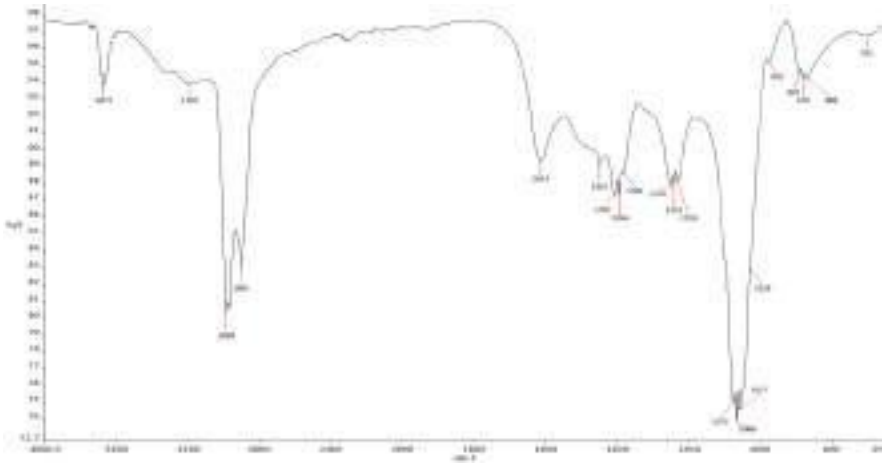


Figure 1. FT-IR absorption spectrum of oligo-(mPD–co-1,3-BD).

ESR assays indicated that there are unpaired electrons in the "base" of the polymer that are associated with the nitrogen elements within the polymer. The bond strength for the quasi-free radicals is lower than that of DPPH, which allows the radical electron to have a partial delocalization. Conductivity data indicate that this polymer has moderate conductivity. SEM analysis revealed a synthesized compound with nanoparticles, indicating uniform polymer growth and good processability. Furthermore, TGA indicates that the compound has good thermal stability.

Together, these data confirm the successful synthesis of a polyfunctional, soluble, and conductive oligomer. The combination of structural characterization, radical behavior, electrical properties, and morphological features reveals the potential of this material for advanced functional applications.

Conclusion

Oligomer base m-phenylenediamine and resorcinol were successfully synthesized through oxidative polymerization in an acidic medium under ultrasonication, using potassium persulphate as oxidizing agent. The FTIR and NMR analyses confirmed the formation of the polymer backbone, while ESR results indicated the presence of electroactive radical species. TGA demonstrated satisfactory thermal stability, and SEM revealed a relatively uniform morphology. Overall, the obtained results highlight the potential of these materials for application in conductive and polyfunctional systems.

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Date despre autori:



Ramil RZAYEV, cercetător științific superior,
Institutul de Chimie al Universității de Stat din Moldova
e-mail: ramilrzayev81@gmail.com
ORCID: 0000-0003-4455-0226



Natalia SUCMAN, Institutul de Chimie, Universitatea de Stat din Moldova, Chișinău, Republica Moldova
e-mail: natalia_sucman@yahoo.com
ORCID: 0000-0001-8733-3040



Mammadov BAKHTİYAR, Doctor în științe chimice, profesor cercetător, director, Institute of Polymer Materials, Azerbaijan National Academy of Sciences, Azerbaijan Republic
e-mail: bazisaley@mail.ru
ORCID: 0000-0001-6135-832X



Fliur MACAEV, Membru corespondent al AȘM, doctor habilitat în științe chimice, Institutul de Chimie al Universității de Stat din Moldova, profesor cercetător
e-mail: fliur.macaev@sti.usm.md
ORCID: 0000-0002-3094-1990