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Synthesis of conducting polymer by gamma Co-60 ray in aqueous solution

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Abstract: This report presents the findings of a study on the synthesis of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) using gamma Co-60 radiation in an aqueous solution saturated with N_2 gas, containing 5 mM EDOT monomer and 0.2 M isopropanol. Gamma radiation with doses ranging from 12 kGy to 58 kGy from a gamma Co-60 source was employed. To assess the chemical composition of the solution before and after irradiation, UV-Vis and FTIR absorption spectra were examined. The results indicated the formation of yellow suspensions in the solution after irradiation, along with the emergence of dimers, oligomers, and PEDOT polymers as evidenced by UV-Vis spectra. The dried powders obtained from the irradiated solutions confirmed the successful synthesis of PEDOT, exhibiting distinct chemical structural characteristics in the FTIR spectra. These findings demonstrate the effective radiation-induced synthesis of conducting PEDOT polymer using gamma Co-60 irradiation.

Keywords: *Radiation synthesis, conducting polymer, PEDOT, gamma irradiation*.

I. INTRODUCTION

Conducting polymers (CP) with unique π-conjugated structures has attracted significant interest in the field of organic electronic materials technology. These polymers have found diverse applications in the production of electronic devices including electroluminescent diodes, photovoltaic cells, and sensors [1]. Poly(3,4-ethylenedioxythiophene) polymers (PEDOT) are widely recognized as one of the most prominent CP due to their easy synthesis, good environmental stability, and high electrical conductivity [2].

Numerous laboratories worldwide have undertaken research pertaining to the PEDOT synthesis with high purity, low cost, and the ability to manufactured on a large scale. Chemical oxidative polymerization and electrochemical polymerization are the two primary technologies presently employed [3, 4].

In literature, PEDOT synthesis involves the oxidation-polymerization of 3,4-ethylenedioxythiophene (EDOT) monomers followed by coupling reactions at the α, α' positions (Scheme 1). The presence of ether groups at the β, β′ positions of thiophene rings, known

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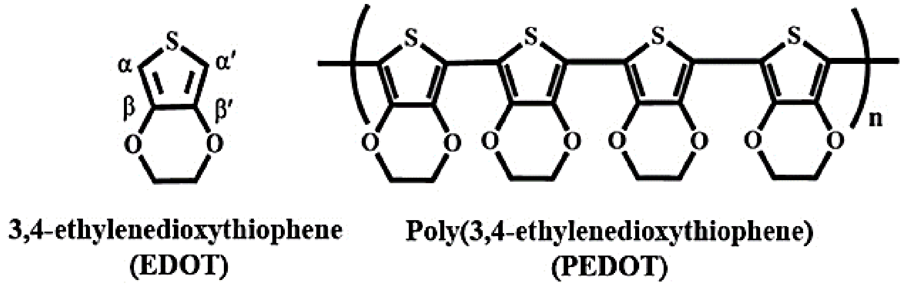
for their strong electron donor effect, significantly increases the reactivity to the free α, α′ locations, and inhibits the development of parasite α-β′ linkages during the polymerization process. The utilization of chemical method for oxidation-polymerization offers obvious advantages, particularly in the synthesis of PEDOT. Nevertheless, the use of oxidizing agents like sodium or potassium persulfate, as well iron (III) salts such as $FeCl_3$ and $Fe_2(SO_4)_3$ [4, 6-8], in this procedure frequently leads to a decrease in the purity of the product.



Scheme 1. Chemical structures of 3,4-ethylenedioxythiophene (EDOT) and poly(3,4-ethylenedioxythiophene) (PEDOT)

Electrochemical polymerization typically involves the utilization of three distinct electrodes, including the counter electrode, reference electrode, and working electrode. On the working electrode, polymers would be deposited throughout the procedure. Polymerization at the working electrode is a half reaction of a redox reaction. The other half reaction is the reduction of protons to hydrogen gas at the counter electrode [9]. The electrochemical polymerization mechanism is outlined as follows: monomers undergo oxidation to form cation radicals that have a relatively high level of stability. The combination of two cation radicals or the combination of a cation radical with a monomer, followed by the sequential removal of two protons, results in the production of a dimer. The process of oxidation and subsequent linkage of dimers remains, resulting in the formation of oligomers. PEDOT is the result of carrying out the same procedure with oligomers. Typically, electrochemical polymerization is employed to produce thin films or standalone films on conductive substrates [10]. However, the substrate requirement for electrochemical polymerization limits its applications.

While electrochemical and chemical oxidative polymerization methods are widely acknowledged and often employed, some challenges persist, including chemical pollution and decreased purity resulting from the utilization of catalysts. Therefore, the utilization of ionizing radiation, particularly γ rays or accelerated electron beams, for the polymerization of PEDOT is regarded as an innovative, an easy and green synthesis method [11]. The utilization of minimal chemical substances, the ability to control the polymerization process, attainment of elevated product purity, and the capacity to generate water-soluble PEDOT, hence enhancing the range of potential applications, have been identified as key factors of this new approach [12].

Currently, there have been studies reporting on the polymerization process of poly(3,4-ethylenedioxythiophene) (PEDOT) utilizing ionizing radiation under different conditions. These researches have investigated the synthesis of PEDOT through gamma radiation-induced oxidation polymerization route, employing different oxidizing agents such as hydroxyl radicals (HO•), azide radicals ($\bullet N_3$), dichloromethyl ($CHCl_2\bullet$) và chloromethyl ($CH_2Cl\bullet$) or by gamma rays in neutral and extremely acidic environments (pH ≈ 0) or in aqueous and organic solvents (CH_2Cl_2) [5, 11-13].

When γ-irradiation of deoxygenated aqueous solutions (under N_2 gas) is conducted at neutral pH, it results in the following chemical species within a nanosecond timescale [14, 15]:

$$H_2O \rightarrow HO\bullet + H\bullet + e_{aq}^- + H_3O^+ + H_2O_2 + H_2$$

In which, radiolytic yields (G) of hydroxyl radical HO•, hydrogen atoms H• and hydrated electron e_{aq}^- are well-known [17, 18]:

$$G_{\mathrm{HO}\bullet} = 2.8 \times 10^{-7}\, molJ^{-1} \quad G_{\mathrm{H}\bullet} = 0.6 \times 10^{-7}\, molJ^{-1} \quad G_{\mathrm{e}_{aq}^{-1}} = 2.8 \times 10^{-7}\, molJ^{-1}$$

Hydroxyl radicals (HO•) are potent oxidizing agents with a redox potential $\mathrm{E}^0_{\mathrm{ESH}}(\mathrm{HO}\bullet/\mathrm{H_2O}) = 2.3\ \mathrm{V_{ESH}}$ at pH = 7, while hydrated electron, e_{aq}^-, are strong reducing species (– 2.8 V_{ESH}) [16]. However, in the presence of isopropanol in solution, HO• is converted into isopropanol radical, $(CH_3)_2C\bullet OH$ [17, 18]. The isopropanol radical, $(CH_3)_2C\bullet OH$, is incapable of oxidizing or reducing the EDOT monomer [5]. Therefore, it is possible that the hydrated electrons, e_{aq}^- or hydrogen atoms, H•, react onto EDOT monomers to form PEDOT polymer.

The reactions of hydrated electron and the hydrogen atom towards thiophene (Th) in aqueous solutions have been studied by pulsed radiolysis [19]. The reaction between H• and thiophene with a rate constant $k(H\bullet + Th) = 9 \times 10^9\ M^{-1}s^{-1}$, and the reaction rate of e_{aq}^- with thiophene is quite slow, $k(e_{aq}^{-1} + Th) = 4 \times 10^7\ M^{-1}s^{-1}$. The presence of the thiophene anion was not detected within the solvated electron systems. This study showed that in both e_{aq}^{-1}/Th and $H\bullet/Th$ systems in the pH range 2 to 11, the 2-hydrothienyl radical was formed. The 2-hydrothienyl radicals can then react with each other (recombination) or react with thiophene, and then eliminate H_2 to generate 2,2'-biothiophene (α,α'-bithiophene) which absorbs at 300 nm.

In Vietnam, there have previously been a few projects using PEDOT for application purposes, such as: researching the fabrication and properties of solar cells using the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)/graphene quantum dots/ nanostructured Si material/light-emitting plasmonic layer consisting of nano-sized gold particles [20], research synthesis and characterization of Ag/PEDOT:PSS films for their potential application as an NH_3 gas sensor [21], or some research directions on applying PEDOT in OLED manufacturing.

II. CONTENT

A. Materials and Methods

1. Chemical and preparation of solution

3,4-ethylenedioxythiophene (EDOT) (≥98%, ThermoFisher Scientific) served as the monomer, and distilled water was used as the solvent. Prior to irradiation, aqueous solutions were degassed with N_2 gas. Additionally, isopropanol was employed as a scavenger of hydroxyl radicals (HO•) generated during the radiolysis of water, preventing the synthesis of PEDOT through oxidative polymerization reactions caused by these radicals.

Aqueous solutions containing 5 mM of EDOT monomer were prepared at room temperature. Subsequently, 0.2 mol. L^{-1} of isopropanol was introduced into the EDOT aqueous solutions, followed by degassing with N_2 for a duration of 20 minutes. These solutions were then stored in the dark to preclude any photochemical reactions and subjected to irradiation using a Co-60 source at the Research and Development Center for Radiation Technology - Danang branch, with a dose range varying from 12 kGy to 58 kGy [12], at a dose rate of 5.8 $kGy.h^{-1}$.

2. Research methods

The EDOT monomer (before irradiation) and radiosynthesized PEDOT (after irradiation) materials were investigated for their chemical structure properties by UV-Vis absorption spectroscopy (Jasco V-730) and Fourier transform infrared (FTIR) spectroscopy (Jasco FTIR-6800).

B. Results

1. UV-Vis absorption spectrum

Upon comparing the solution's color before and after irradiation, a distinct color change was observed. EDOT samples after irradiation showed the presence of a yellow suspension and turbidity that gradually increased with radiation dose from 12 kGy to 34 kGy. Interestingly, at a radiation dose of 58 kGy, the color change reversed, becoming lighter (as illustrated in Fig. 1).

Fig. 1. Photographs of EDOT samples at concentration of 5mM before and after irradiation at doses 12 kGy, 23 kGy, 34 kGy and 58 kGy under N_2 in the presence of 0.2 M isopropanol

The UV-visible absorption spectrum of aqueous solution containing 5mM in EDOT monomer exhibits two prominent absorption peaks at 239 nm and 256 nm as shown in Fig. 2. The absorption of light in the UV-Vis region by the pure thiophene molecule occurs within the wavelength range of 225 nm to 246 nm, this absorption is attributed to the $\pi \rightarrow \pi^*$ electronic transition [22]. Consequently, the presence of two distinct absorption peaks in the EDOT monomers can be ascribed to the $\pi \rightarrow \pi^*$ electronic transition within the thiophene ring.

In the UV-Vis absorption spectra of EDOT solutions after irradiation, a notable trend becomes apparent. Specifically, there is a pronounced disappearance of the maximum absorption peak at 239 nm, particularly noticeable at radiation doses exceeding 12 kGy. Concurrently, a subtle shift is observed in the maximum absorption peak at 256 nm, with changes corresponding to the increasing radiation dose. To provide specific details, these shifts are as follows: 256 nm (12 kGy), 257 nm (23 kGy), 258 nm (34 kGy), and 267 nm

(58 kGy). The emergence of these absorption peaks serves as evidence for the possible presence of EDOT monomers in the solution after irradiation. However, in all UV-Vis spectra of the solutions after irradiation, absorption peaks appear at about 355 nm. These absorption peaks demonstrate the formation of EDOT dimers in solution [12]. In this study, we observe that spectra exhibit a distinctive feature of continuous scattering within the wavelength range of 400-600 nm. This scattering is attributed to the presence of longer oligomers and polymers of PEDOT [23-25]. Interestingly, this scattering phenomenon is absent in the UV-Vis spectrum of EDOT monomers before irradiation.

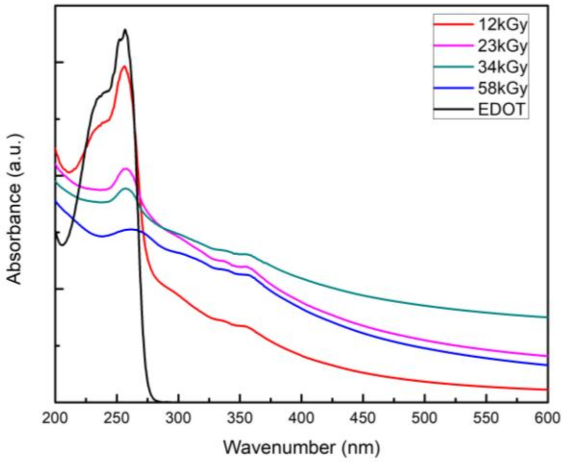


Fig. 2. Absorption spectra of an aqueous solution containing 5mM in EDOT before irradiation and after irradiation at doses 12 kGy, 23 kGy, 34 kGy and 58 kGy under N_2 in the presence of 0.2 M isopropanol

2. FTIR absorption spectrum

The solution samples obtained after irradiation were subsequently dried under room conditions to yield powdered samples suitable for FTIR spectroscopy analysis.. The results of FTIR spectra of radiosynthesized PEDOT dried powder samples and EDOT monomer are shown in Fig. 3.

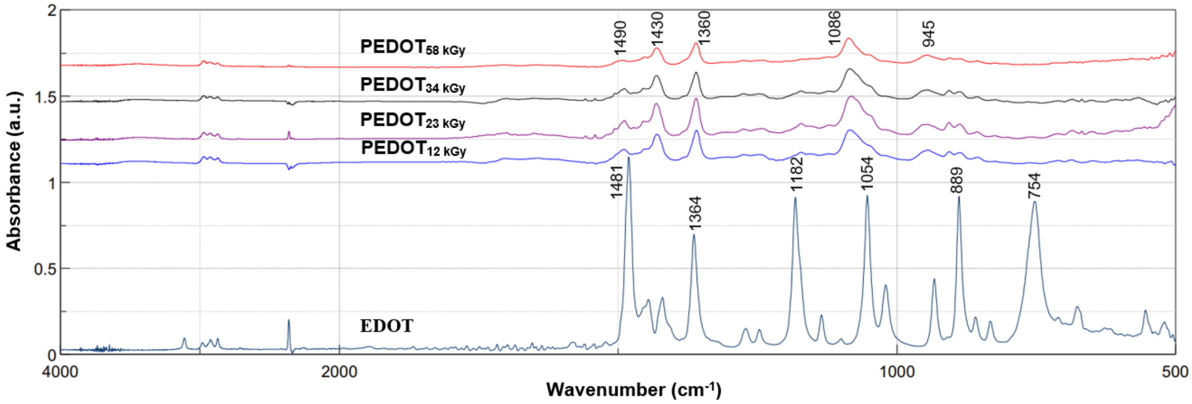


Fig. 3. FTIR spectra of pure EDOT monomer before irradiation and PEDOT powders obtained by radiation-induced polymerization at doses 12 kGy, 23 kGy, 34 kGy and 58 kGy

Between 1500 and 500 cm^{-1}, the FTIR absorption spectra of the EDOT monomer and the PEDOT powder samples are consistent with previous reports [12, 26, 27]. For EDOT monomer, the absorption bands at 889, 1054 and 1182 cm^{-1} correspond to the stretching vibrations of ethylenedioxy group (C–O–R–O–C). The stretching vibrations of C–C and C=C in thiophene ring are also observed at 1364 and 1481 cm^{-1} [26].

For PEDOT powders, the absorption bands at around 1360, 1430 and 1490 cm^{-1} characterize the C–C and C=C stretching modes in the thiophene [27] can be seen in the FTIR spectra (Fig. 3), while the vibrations observed at about 1275, 1245, 1170 and 1084 cm^{-1} are assigned to the stretching modes of the ethylenedioxy group (C–C and C–O–R–O–C). The vibrations of C–S in the thiophene ring can be observed at 945 cm^{-1} and 906cm^{-1} [12]. The absorption peak of 754 cm^{-1}, which is attributed to the out-of-plane bending vibration of the C–H bond at the α, α' position, appears in the EDOT spectrum but completely disappears after irradiation in all the FTIR spectrum of the PEDOT powders.

C. Discussion

The irradiation of 5 mM EDOT samples under N_2 in the presence of 0.2 M isopropanol at different radiation doses through UV-Vis spectroscopy demonstrated the formation of PEDOT oligomers and polymers through the free radical mechanism. However, this study has yet to elucidate the primary agent responsible for reacting with EDOT monomers, as well as the ideal radiation dose required for the complete conversion of all EDOT monomers, despite the observation of dark yellow post-irradiation solutions. To address these questions, further investigations should be conducted using EDOT samples at a concentration of 1 mM to assess the maximum radiation dose [1].

The FTIR spectra proved that the powder samples obtained after irradiation were PEDOT polymer. The absorption bands of the radiosynthesized PEDOT in this investigation exhibit resemblances to the absorption bands observed in earlier studies on radiation-polymerized oxidized PEDOT samples [1, 12]. Significantly, the absence of the 754 cm^{-1} absorption band provides additional evidence for the radiation synthesis of PEDOT via coupling processes occurring at the α, α' positions.

The FTIR spectrum of the dry powder sample of PEDOT, synthesized via oxidation polymerization by hydroxyl radical HO•, shows the appearance of the characteristic O-H bond absorption band along the polymer chain at about 3600 - 3200 cm^{-1}. This observation provides strong evidence that PEDOT exhibits high solubility in aqueous solutions due to the presence of hydroxyl radicals [12]. However, upon comparing the Fourier Transform Infrared (FTIR) spectra acquired in this investigation, it is evident that the presence of distinctive O-H bond absorption is not observed. Consequently, it becomes imperative to conduct solubility experiments to assess the solubility characteristics of the samples synthesized in this particular study and determine how they may differ from previous observations.

III. CONCLUSIONS

The successful synthesis of PEDOT from the EDOT monomer using Co-60 gamma radiation has been confirmed through the application of UV-Vis and FTIR spectroscopic techniques. To further advance this research, additional investigations are warranted to ascertain the optimal radiation dose, solubility conditions, and procedural parameters for the synthesis of PEDOT using radiation. Additionally, exploring the most favorable conditions and techniques for this synthesis process will be crucial for achieving enhanced results and refining the methodology.

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