

Synthesis and characterization of novel poly[4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione]

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Abstract

By the oxidative coupling polymerization, a new polythiophene containing 1,2,4-triazole heterocyclic group was synthesized in chloroform solvent using iron(III) chloride as an oxidant catalyst. Analyses of infrared (IR) and ultraviolet-visible (UV-Vis) spectra confirmed that the polymerization reaction took place and the absorption band at 469 nm characterized for π - π^* transition in the conjugated polymer. Morphology and surface properties of the polymer were studied by field emission scanning electron microscopy (FESEM). Polymer had relatively uniform size distribution. Based on thermal gravimetry analysis (TGA), polymer is without impurities and has an adequate thermal stability in air atmosphere when completely decomposed at 500 °C. The polymer exhibited fluorescence emissions at 596 nm corresponding to the conjugated chain in polymer. Polymer exhibited a good electrical conductivity in the undoped state (around $1.37\text{E}-7\text{ S.cm}^{-1}$ at 1 MHz).

Keywords. Polythiophene, 1,2,4-triazole, chemical polymerization, heterocyclic side groups, electrical conductivity.

1. INTRODUCTION

Based on the capability in advanced electronic, ionic conductivity and optoelectronic applications, the synthesis and characterization of polymers having heterocyclic units have been commonly studied.^[1-3] Polythiophenes and their derivatives have attracted considerable attention because of their good environmental stability, simplicity of structural modification, versatility optical and electrochemical properties. They can be used as active materials in the advanced technologies of electrochromic and electronic devices, for example, organic light

emitting diodes (OLEDs),^[4,5] organic photovoltaic (OPV) cells,^[6,7] organic field effect transistors (OFETs)...^[8] Most polythiophenes display remarkable optical properties such as thermochromism,^[9,10] photochromism^[11] and biochromism.^[12] In addition, they can be applied in water-soluble sensing agents for the recognition of DNA, proteins, metal ions and small biosensors on the modifications in photoluminescence and UV-Vis spectroscopy investigations.^[13-15]

For the first time, the applications of unsubstituted polythiophenes were restricted because of its insolubility in water and water-miscible solvents, as

well as medium electrical conductivity. However, these limitations were improved by substituting alkyl or alkoxy substituent and heterocyclic side substituent to the thiophene ring at position 3, such as poly(3-alkylthiophenes), poly(3-alkoxythiophenes),...^[16] It is also widely known that the electroluminescence of π -conjugated polymers is caused by recombination of electrons that promoted to the conduction bands and holes injecting into the valence band to make singlet excitons.^[17] In light-emitting diodes, the combination of an electron-transporting (ET) material between the polymer layers and the cathode can lead to the increase in the power efficiency via simplified injection of electron from the cathode. A numerous of compounds containing electron-deficient as quinoxaline, triazine, triazole and oxadiazole have been studied as ET materials.^[18-21] For example, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was used widely in such materials.^[22] However, considerations have been changed to nitrogen-containing heterocycles including 1,2,4-triazoles, 1,3,5-triazines and quinoxalines because oxadiazoles were not totally effective ET materials and 1,2,4-triazoles show more efficiently *hole-blocking* properties than PBD.^[23-25]

There are a lot of researches in synthesis of polythiophenes with 3-substituted derivatives bearing heterocyclic side groups containing nitrogen atom. For example, Ho *et al.* investigated new cationic polythiophene derivatives containing 1-methylimidazolium ion using for colorimetric and fluorometric detection of nucleic acids.^[26] Another high-regioregular polythiophene derivatives containing 1-methylimidazolium ion were synthesized by Bondarev *et al.*^[27] Besides, in 2010, poly[3-(6-pyridiniumylhexyl)thiophene bromide] (P3PHT⁺ Br⁻) from poly[3-(6-bromohexyl)thiophene] was synthesized by Rider *et*

al.^[28] Giri *et al.* had synthesized poly(3-benzyl-1,2,3-triazole thiophene) and studied characterization of this polymer on the basis of reusable fluorescent probe for the recognition of trace nitroaromatics.^[29] In our previous studies, we have synthesized two new polythiophenes containing 1,2,4-triazole heterocycle^[30] and 2-thioxo-1,3-thiazolidin-4-one heterocycle^[31] having the good solubility in DMSO. Therefore, it is of interest to prepare polythiophenes carrying other heterocyclic side groups.

This paper reported the synthesis of novel poly[4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione] containing the 1,2,4-triazole heterocycle on the side chain in poly(3-alkylthiophene): This one had an ET component which have the good capability of *receiving electrons* was synthesized by chemical oxidative coupling method. The properties of new polymer are characterized by SEM, TGA methods, photoluminescence and photoluminescence emission spectra. The electrical conductivity of polymer without doping was studied over the frequency range of 100Hz–1MHz.

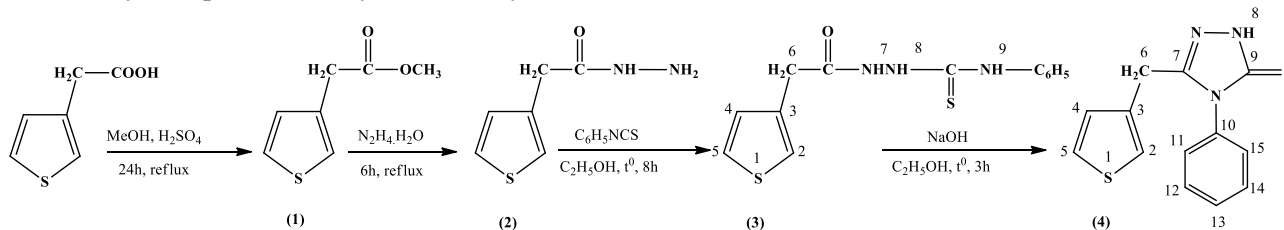
2. MATERIALS AND METHOD

2.1. Materials

The starting chemicals, such as 3-thiophene acetic acid (Sigma Aldrich), methanol (Merck), phenylisothiocyanate (Merck), hydrazine hydrate (Merck), were used without further purification.

2.2. Synthesis of poly[4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione]

2.2.1. Synthesis of 4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione



Scheme 1: Synthesis of 4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Methyl 2-(thiophen-3-yl)acetate **1** and 2-(thiophen-3-yl)acetohydrazide **2** were synthesized according to our previous researches.^[32,33]

- Synthesis of *N*-phenyl-2-(2-(thiophen-3-yl)acetyl)hydrazinecarbothioamide (**3**)

A mixture of **2** (10 mmol), phenylisothiocyanate (10 mol) and 30 mL of ethanol (96 %, Vietnam) was refluxed at 80 °C for 8 h. Precipitated solids were filtered and recrystallized from ethanol to give the white crystals (yield: 80 %, m.p. 143 °C). IR (KBr, ν , cm⁻¹): 3512, 3424 (NH), 3048, 2954 (C–H), 1666

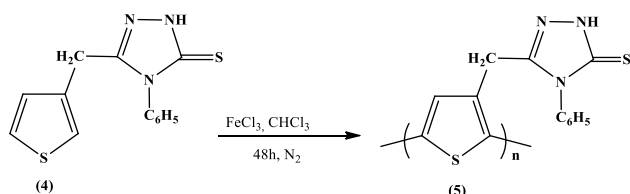
(C=O), 1562 (C=C), 1226 (C=S). ¹H-NMR (DMSO-*d*₆, δ, ppm; *J*, Hz): 7.16-7.18 (*m*, 1H, H-2); 7.09 (*d*, *J*₅₋₄ 5.0 Hz, 1H, H-4); 7.47 (*dd*, *J*₂₋₅ 3.0 Hz, *J*₄₋₅ 4.5 Hz, 1H, H-5); 3.54 (*s*, 2H, H-6); 9.58-10.10 (1H, H-7, H-9); 7.33-7.44 (aromatic protons).

- *Synthesis of 4-phenyl-3-(thiophen-3-ylmethyl)-1H-1,2,4-triazole-5(4H)-thione (4)*

The mixture of **3** (1.4 mmol), 10 mL of ethanol and NaOH 10 % (1.25 mmol) was refluxed at 80 °C for 3 h. After cooling, the reaction mixture was neutralized by HCl 10 % to pH = 1-2. The product was separated by filtration and purified by recrystallization in ethanol to give 1.42 g of **4** as pale yellow crystals (yield: 52%; m.p. 178 °C).^[33] IR (KBr, ν, cm⁻¹): 3453 (NH), 3088, 2911 (C-H), 1576 (C=C thiophene), 1278, 1207 (C=S). ¹H-NMR (DMSO-*d*₆, δ, ppm; *J*, Hz): 6.96 (*m*, 1H, H-2); 6.75 (*d*, *J*₅₋₄ 5.0 Hz, 1H, H-4); 7.38 (*dd*, *J*₂₋₅ 3.0 Hz, *J*₄₋₅ 5.0 Hz, 1H, H-5); 3.85 (*s*, 2H, H-6); 13.77 (*s*, 1H, H-8), 7.26-7.28 (*m*, 2H, H-11, H-15); 7.48-7.50 (*m*, 3H, H-12, H-13, H-14). ¹³C NMR [*d*₆-DMSO, ppm]: 123.86 (C2), 134.24 (C3), 128.02 (C4), 126.14 (C5), 26.35 (C6), 150.83 (C7), 167.85 (C9), 133.55 (C10), 128.16 (C11 and C15), 129.20 (C12 and C14), 129.34 (C13).

2.2.2. *Synthesis of poly[4-phenyl-3-(thiophen-3-ylmethyl)-1H-1,2,4-triazole-5(4H)-thione]*

Polymer **5** was synthesized by oxidative coupling polymerization method utilize dry chloroform using 4 molar equivalents of anhydrous ferric chloride.^[34,35] FeCl₃ (8 mmol) was stirred in chloroform (40 mL) for 15 minutes under nitrogen atmosphere. Afterwards, the solution of monomer **4** (2 mmol) in 20 mL chloroform was prepared and added slowly to the solution containing FeCl₃. Then, the polymerization mixture was further stirred for 48 h at room temperature under nitrogen atmosphere. The precipitate was filtered and washed several times with methanol and deionized water.



Scheme 2: Synthesis of poly[4-phenyl-3-(thiophen-3-ylmethyl)-1H-1,2,4-triazole-5(4H)-thiones]

Polymer **5** was purified via Soxhlet extraction with methanol for 48h to remove residual FeCl₃ and

oligomers. Finally, polymer **5** was repeatedly washed with methanol, and vacuum-dried to get dark orange-colored powder (yield: 82%). IR (KBr, ν, cm⁻¹): 3417 (NH), 3062-2917 (C-H), 1629 (conjugated C=C-C=C), 1495, 1424 (C=C thiophene), 1592 (C=C benzene).

2.3. Methods

Melting points were measured in the opening in a capillary tubes using a Gallenkamp Melting Point Apparatus. IR spectra were recorded using a Nicolet Impact 410 FTIR Spectrometer (USA) on KBr pellets of polymer powders mixed with KBr. NMR spectra were recorded on a Bruker XL-500 Spectrometer (USA) at 500 MHz using DMSO-*d*₆ and CDCl₃ as solvents. The TGA thermograms were measured on a Shimadzu Simultaneous Measuring Instrument, DTG-60/60H, at a heating rate of 10 °C/min in the temperature range of 30-600 °C in air. The SEM analysis was performed using SEM-Hitachi-4800 (Japan). The UV-Vis spectra were recorded using a UV-visible spectrophotometer (GBC, Cintra 40, USA and Jasco, V670, Japan). The photoluminescence and photoluminescence emission spectroscopy were measured on Horiba Fluoromax Series (American). The electrical conductivity of the sample in the form of 0.5 cm diameter tablets was determined using the Agilent E4980A Precision LCR Meter (United States).

3. RESULTS AND DISCUSSION

3.1. FT-IR spectra

Monomer **4** was chemically polymerized using FeCl₃ as oxidant to synthesize the corresponding polymer **5**. Structure and formation of conjugated-π polythiophene of polymer was determined based on FT-IR spectra. An assessment of the change of the vibrational modes occurring on polymer and monomer has a role to explain the experimental absorption spectra.

The synthesized polymer exhibited absorption bands in the same locations as its precursor monomer. In addition, the bands of polymer were obviously extended in comparison with those of monomer, principally depend on the wide chain dispersity of the resulting oligomers and polymers.^[36] In the IR spectrum of polymer **5**, there are still the bands at about 1592 cm⁻¹ belonging to asymmetric vibrations of C=C bonds in benzene ring; the bands at 1495 and 1424 cm⁻¹ belonging to asymmetric vibrations of carbon-carbon bonds in thiophene ring; and the bands

at 691 cm^{-1} attributed to out-of-plane bending vibrations of C-H bond in benzene ring.

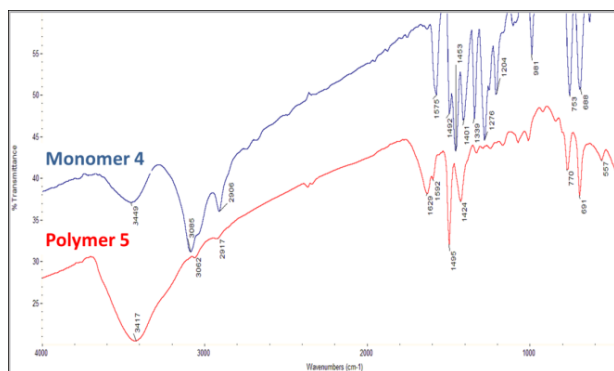


Figure 1: IR spectra of monomer 4 and polymer 5

However, the comparison to the IR spectrum of monomer showed that the intensities of the bands at about $3062\text{--}2917\text{ cm}^{-1}$ in the IR spectrum of polymer 5 decreased because the replacement of the C–H bonds in thiophene ring of the monomer 4 (bands at 3085 and 2906 cm^{-1} , respectively) by new C–C bonds to make polymer 5. This evidence indicated that during the free radical polymerization, the aromaticity of thiophene ring was retained and that polymerization reaction took place at the 2,5-positions of the thiophene ring.^[35,37] A new absorption band that appeared at 1629 cm^{-1} with strong intensity, characterized to the conjugated C=C–C=C in polymer. Moreover, a strong and wide stretching band in the $3500\text{--}3400\text{ cm}^{-1}$ region is characterized for the stretching vibration of the intermolecular hydrogen bonds of N–H.

3.2. TGA

The thermal stability of the polymers is an important parameter for many applications in dye materials or solar cells. To examine the thermal stability of polymer 5, the thermal analysis was performed from 25 to $600\text{ }^{\circ}\text{C}$ under air. The TGA and DTA curves of the obtained polymer is shown in figure 2. The polymer 5 is completely decomposed when heated to $500\text{ }^{\circ}\text{C}$ in air atmosphere. The first stage ranges between room temperature and $100\text{ }^{\circ}\text{C}$, mainly due to the evaporation of water. In the second stage from 200 to $500\text{ }^{\circ}\text{C}$, the main weight loss of polymer is 94.56% corresponding to the decomposition of polythiophene chains. Above $500\text{ }^{\circ}\text{C}$, polymer has completely decomposed. In addition, only one exothermic peak which appeared at $472\text{ }^{\circ}\text{C}$ in the DTA curve can show that polythiophene was degraded only in one stage. This evidence proves that obtained polymer was without any impurities.

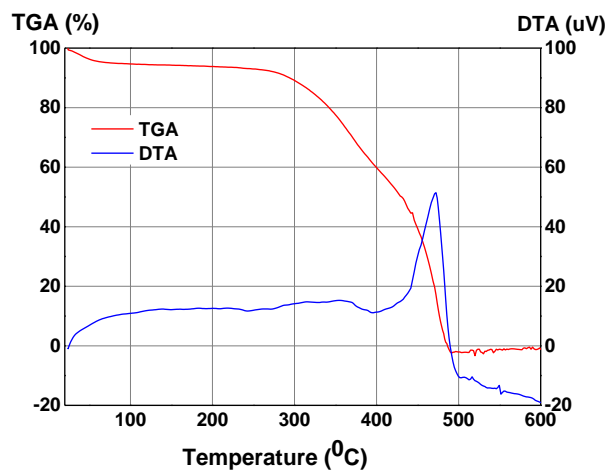


Figure 2: TGA/DTA thermogram of polymer 5

3.3. FE-SEM

FE-SEM image of polymer is shown in figure 3. The morphology of polymer 5 displays a granular isotropic and flake morphology with size more than $5\text{ }\mu\text{m}$. Densely packed particles of polymer with relatively uniform size distribution are observed.

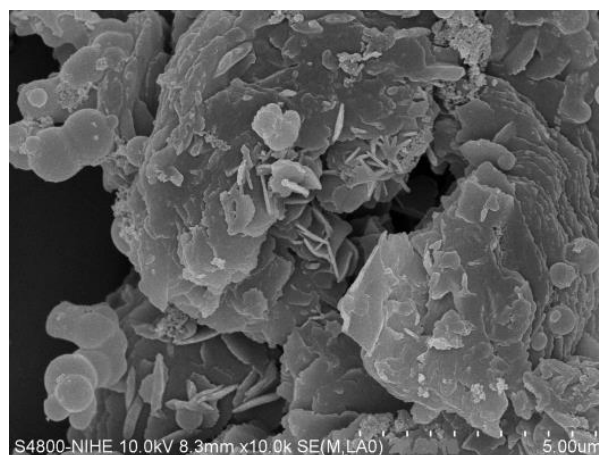


Figure 3: FE-SEM image of polymer 5

3.4. UV-Vis spectra

The UV-Vis spectra of the polymer in the DMSO solution and in a pellet containing polymer powder were measured and shown in Figure 4. It can be seen the maximum absorption band at 286 nm in the UV-Vis spectra of polymer 5 in DMSO solution was according to $S_0 \rightarrow S_1$ ($n\text{--}\pi$) transition of the conjugated polythiophene, which is caused by semi-twisted conformation^[35] or phenyl conjugated side chains of polythiophene.^[38] In DMSO solution, the polymer presents a maximum absorption band at 382 nm , which is attributed to the $\pi\text{--}\pi^*$ transition in the conjugated polythiophene main chains; while in solid

state, the peak is at 469 nm. It presents the similar results in comparison with other polythiophenes.^[29,39,40] The 87 nm shift to longer wavelength could assign to the π - π^* transition in the π -conjugated backbone which was caused by the interchain π - π stacking and intermolecular interactions in solid state.

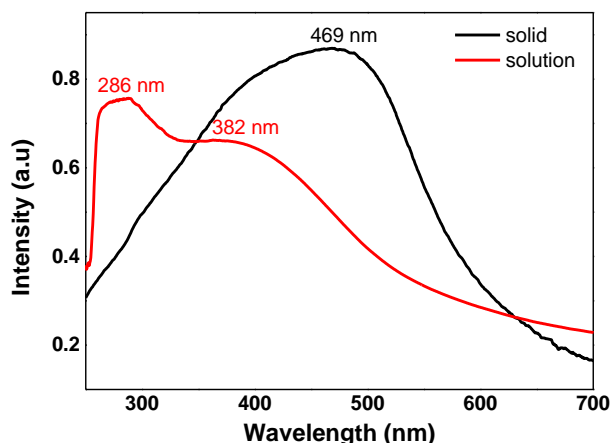


Figure 4: UV-Vis spectra of polymer **5** in DMSO (solution) and in pellet (solid)

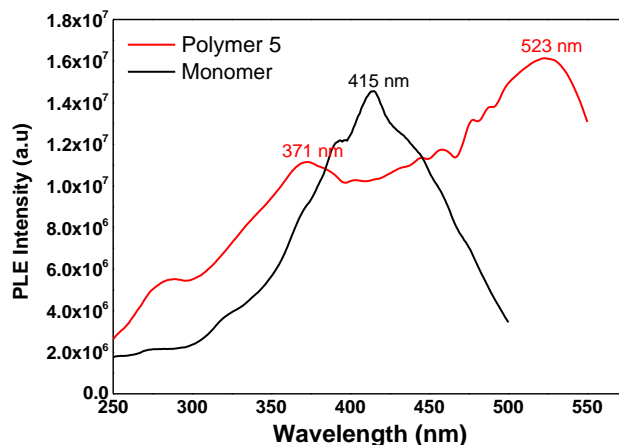
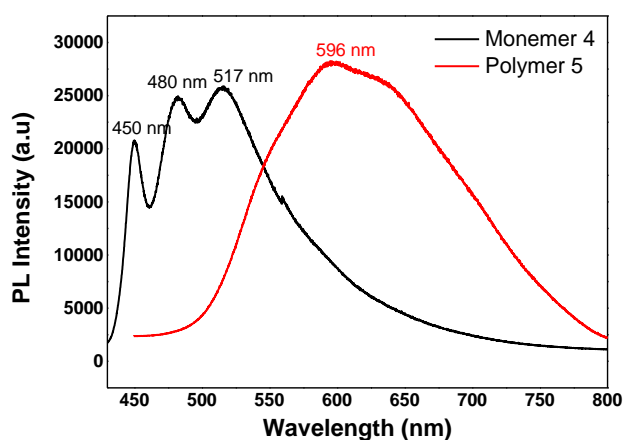


Figure 5: Photoluminescence and photoluminescence emission spectra of polymer **5** and monomer **4**

3.6. Electrical conductivity

Figure 6 shows the electrical conductivity of polymer **5** as a function of frequency at room temperature. Electrical conductivity was increased with the increase of frequency. At 1 MHz, the electrical conductivity of polymer was 1.37×10^{-7} S/cm. In comparison, the conductivity of undoped polythiophene was observed to be between 10^{-7} and 10^{-6} S/cm with a mobility of 10^{-9} to 10^{-8} m²/V/s.^[41] In a later research, the reduced or neutral polythiophene exhibited a conductivity of 1.8×10^{-8} S/cm.^[42] For poly(3-hexylthiophene) – a *p*-type semiconductor polymer is widely used as an electron donor in solar cells, with relatively low conductivity

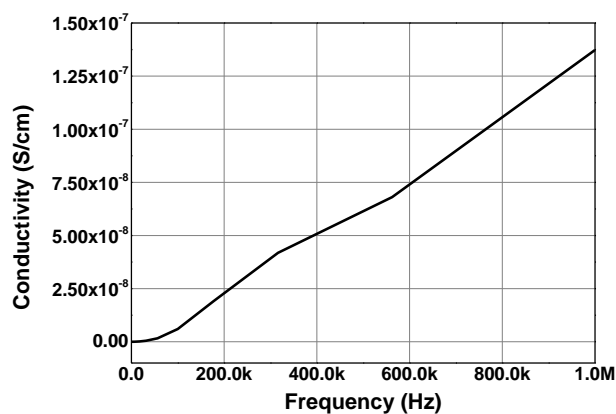


Figure 6: Electrical conductivity of polymer **5**

3.5. Photoluminescence spectra

The analyses of photoluminescence and photoluminescence emission spectroscopies of polymer **5** were carried out and compared with the monomer **4** (figure 5).

The monomer **4** emission peak of photoluminescence spectrum appears in a shorter wavelength range (450, 480 and 517 nm) with 415-nm excitation. Compared with the monomer, polymer **5** exhibited maximum fluorescence emission a longer wavelength (596 nm) with a Stokes shift of 127 nm. Consequently, the formation of conjugated chain length is the main factor that influences the higher emission wavelength of polymer **5**. For comparison purposes, poly(3-benzyl-1,2,3-triazole thiophene) containing 1,2,4-triazole heterocycle on the side chain, synthesized by the same FeCl₃ oxidation method of polymerization, displays the maximum emission peak at 551 nm in the solid state.^[29] The photoluminescence measurements show that the polymer **5** could be used as a fluorescent polymeric dye material.

in the non-doped state ($\sim 10^{-8}$ S/cm) in the frequency range of interest for most electronic applications.^[43] It can be seen that non-doped polymer **5** has a fairly good electrical conductivity when compared to polythiophene or poly(3-hexylthiophene).

4. CONCLUSION

In this work, poly[4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione], a novel polythiophene derivative containing the 1,2,4-triazole unit on the side chain was synthesized by oxidative coupling polymerization in chloroform solvent using iron(III) chloride as oxidizing agent. IR and UV-Vis spectroscopy investigations confirmed that the polymerization reaction of monomer **4** to form polymer **5** was occurred successfully. The thermal analysis showed that the polymer is medium thermal stability and have been completely purified. Polymer exhibited maximum fluorescence emission at 596 nm and had a good electrical conductivity in the non-doped state, which could be used for fluorescent dye material or an electron transporting material.

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REFERENCES

- J. G. Liu, Y. Nakamura, C. A. Terraza, Y. Shibasaki, S. Ando, M. Ueda. Highly refractive Polyimides derived from 2,8-Bis(*p*-aminophenylsulfanyl)dibenzothiophene and aromatic dianhydrides, *Macromol. Chem. Phys.*, **2008**, 209(2), 195-203.
- N. Fukuzaki, T. Higashihara, S. Ando, M. Ueda. Synthesis and characterization of highly refractive polyimides derived from thiophene-containing aromatic diamines and aromatic dianhydrides, *Macromolecules*, **2010**, 43(4), 1836-1843.
- M. Elbing, A. Garcia, S. Urban, T. Q. Nguyen, G. C. Bazan. *In situ* conjugated polyelectrolyte formation, *Macromolecules*, **2008**, 41(23), 9146-9155.
- J. Pei, W. L. Yu, J. Ni, Y.-H. Lai, W. Huang, A. J. Heeger. Thiophene-based conjugated polymers for light-emitting diodes: Effect of aryl groups on photoluminescence efficiency and redox behavior, *Macromolecules*, **2001**, 34(21), 7241-7248.
- D. R. Baigent, P. J. Hamer, R. H. Friend, S. C. Moratti and A. B. Holmes, Polymer electroluminescence in the near Infra-Red, *Synth. Met.*, **1995**, 71(1-3), 2175.
- T. A. Chen, R. D. Rieke. The first regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) and a regiorandom isopolymer: nickel versus palladium catalysis of 2(5)-bromo-5(2)-(bromozincio)-3-hexylthiophene polymerization, *J. Am. Chem. Soc.*, **1992**, 114(25), 10087-10088.
- P. B. Balanda, M. B. Ramey, J. R. Reynolds. Water-soluble and blue luminescent cationic polyelectrolytes based on poly(*p*-phenylene), *Macromolecules*, **1999**, 32(12), 3970-3978.
- H. Koezuka, A. Tsumura, T. Ando. Field-effect transistor with polythiophene thin film, *Synth. Met.*, **1987**, 18(1-3), 699-704.
- I. Levesque, P. Bazinet, J. Roovers. Optical properties and dual electrical and ionic conductivity in Poly(3-methylhexa(oxyethylene)oxy-4-methylthiophene), *Macromolecules*, **2000**, 33(8), 2952-2957.
- C. Roux, M. Leclerc, Rod-to-coil transition in alkoxy-substituted polythiophenes, *Macromolecules*, **1992**, 25(8), 2141-2144.
- I. Levesque, M. Leclerc. Novel dual photochromism in polythiophene derivatives, *Macromolecules*, **1997**, 30(15), 4347-4352.
- L. Kumpumbu-Kalemba, M. Leclerc. Electrochemical characterization of monolayers of a biotinylated polythiophene: towards the development of polymeric biosensors, *Chem. Commun.*, **2000**, 2000(19), 1847-1848.
- X. Duan, L. Liu, F. Feng, S. Wang. Cationic conjugated polymers for optical detection of dna methylation, lesions, and single nucleotide polymorphisms, *Acc. Chem. Res.*, **2010**, 43(2), 260-270.
- X. Feng, L. Liu, S. Wang, D. Zhu. Water-soluble fluorescent conjugated polymers and their interactions with biomacromolecules for sensitive biosensors, *Chem. Soc. Rev.*, **2010**, 39(7), 2411-2419.
- S. W. Thomas, G. D. Joly, T. M. Swager. Chemical sensors based on amplifying fluorescent conjugated polymers, *Chem. Rev.*, **2007**, 107(4), 1339-1386.
- P. Blanchard, P. Leriche, P. Frere, J. Roncali. Conjugated polymers - Theory, synthesis, properties and characterization (Edited by T. A. Skotheim, J. Reynolds), **2007**, CRC Press, 468.
- A. B. Holmes, D. D. C. Bradley, A. R. Brown, P. L. Burn, J. H. Burroughes, R. H. Friend, N. C. Greenham, R. W. Gymer, D. A. Halliday, R. W. Jackson, A. Kraft, J. H. F. Martens, K. Pichler, I. D. W. Samuel. Photoluminescence and electroluminescence in conjugated polymeric systems, *Synth. Met.*, **1993**, 57(1), 4031-4040.
- M. Stukelj, F. Papadimitrakopoulos, T. M. Miller, S. J. Son. Effects of polymeric electron transporters and the structure of poly(*p*-phenylenevinylene) on the performance of light-emitting diodes, *J. Am. Chem. Soc.*, **1995**, 117(48), 11976-11983.
- M. Stukelj, T. M. Miller, F. Papadimitrakopoulos, I. J. Rothberg. Design and application of electron-transporting organic materials, *Science*, **1995**, 267, 1969-1972.
- M. Thelakkat, R. Fink, P. Posch, J. Ring, H. W. Schmidt. Aromatic polyethers with 1,3,5-triazine units

- as hole blocking/electron transport materials in LEDs, *Polym. Prepr.*, **1997**, 38(1), 323.
21. R. Fink, C. Frenz, M. Thelakkat, H. W. Schmidt. Synthesis and characterization of aromatic Poly(1,3,5-triazine-ether)s for electroluminescent devices, *Macromolecules*, **1997**, 30(26), 8177-8181.
 22. S. J. Chung, K. Y. Kwon, S. W. Lee, J. H. Jin, C. H. Lee, C. E. Lee, Y. Park. Highly efficient light-emitting diodes based on an organic-soluble Poly(*p*-phenylenevinylene) derivative carrying the electron-transporting PBD moiety, *Adv. Mater.*, **1998**, 10(14), 1112-1116.
 23. J. Kido, C. Ohlaki, K. Hongawa, K. Okuyama, K. Nagai. 1,2,4-Triazole derivative as an electron transport layer in organic electroluminescent devices, *Jpn. J. Appl. Phys.*, **1993**, 32(2-7A), L917.
 24. C. Miao, X. Tai, L. Hui-xue, L. Xiang. Preparation and electrochemical properties of 3-Phenyl-6-aryl-1,2,4-triazolo[3,4-b][1,3,4] thiadiazoles, *Chem. Res. In Chinese Uni.*, **2004**, 20(6), 810-812.
 25. S. M. Kelly. Flat Panel Displays: Advanced Organic Materials, *RSC: Cambridge*, **2000**, 232 p.
 26. H. A. Ho, M. Boissinot, M. G. Bergeron, G. Corbeil, K. Dore, D. Boudreau, M. Leclerc. Colorimetric and fluorometric detection of nucleic acids using cationic polythiophene derivatives, *Angew. Chem., Int. Ed.*, **2002**, 41(9), 1548-1551.
 27. D. Bondarev, J. Zednik, I. Sloufova, A. Sharf, M. Prochazka, J. Pflieger, J. Vohlidal. Synthesis and properties of cationic polyelectrolyte with regioregular polyalkylthiophene backbone and ionic-liquid like side groups, *J. Polym. Sci. A: Polym. Chem.*, **2010**, 48(14), 3073-3081.
 28. D. A. Rider, B. J. Worfolk, K. D. Harris, A. Lalany, K. Shahbazi, M. D. Fleischauer, M. J. Brett, J. M. Buriak. Stable inverted polymer/fullerene solar cells using a cationic polythiophene modified PEDOT:PSS cathodic interface, *Adv. Funct. Mater.*, **2010**, 20(15), 2404-2415.
 29. D. Giri, S. N. Islam, S. K. Patra. Synthesis and characterization of 1,2,3-triazole appended polythiophene based reusable fluorescent probe for the efficient detection of trace nitroaromatics, *Polymer*, **2018**, 134, 242-253.
 30. V. Q. Trung, N. N. Linh, V. T. Hoa, T. T. T. Duong, K. Linh. Synthesis of polythiophene containing 1,2,4-triazol five-membered heteroaromatic ring, *Vietnam J. Chem.*, **2015**, 53(6e1,2), 5.
 31. N. N. Linh, T. T. Doan, N. T. Cong, D. K. Linh, J. Pflieger, V. Q. Trung. Synthesis of polythiophene containing 2-thioxo-1,3-thiazolidin-4-one heterocycle, *Vietnam J. Chem.*, **2016**, 54(6e1), 259.
 32. T. V. Quoc, L. N. Ngoc, C. N. Tien, T. P. Chien, L. V. Meervelt. Crystal structure of N-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)-2-(thiophen-3-yl)acetamide, *Acta. Cryst.*, **2017**, 73(6), 901-903.
 33. T. V. Quoc, L. N. Ngoc, D. D. Ba, T. P. Chien, H. N. Huy, L. V. Meervelt. Crystal structure and Hirshfield surface analysis of 4-phenyl-3-(thiophen-3-ylmethyl)-1H-1,2,4-triazole-5(4H)-thione, *Acta. Cryst. E*, **2018**, E74(6), 812-815.
 34. K. ByoungSuhk, C. Li, G. Jianping, O. Yoshihito. Titration behavior and spectral transitions of water-soluble polythiophene carboxylic acids, *Macromolecules*, **1999**, 32(12), 3964-3969.
 35. B. X. Valderrama-García, E. Rodríguez-Alba, E. G. Morales-Espinoza, K. M. Chane-Ching, E. Rivera. Synthesis and characterization of novel polythiophenes containing pyrene chromophores: thermal, optical and electrochemical properties, *Molecules*, **2016**, 21(2), 172, 18 pages.
 36. B. Lu, J. Yan, J. Xu, S. Zhou, X. Hu. Novel electroactive proton-doped conducting poly(aromatic ethers) with good fluorescence properties via electropolymerization, *Macromolecules*, **2010**, 43(10), 4599-4608.
 37. K. Lin, S. Zhang, H. Liu, Y. Zhao, Z. Wang, J. Xu. Effects on the electrochemical and electrochromic properties of 3 linked polythiophene derivative by the introduction of polyacrylate, *Int. J. Electrochem. Sci.*, **2015**, 10, 7720-7731.
 38. Y. Zou, W. Wu, G. Sang, Y. Yang, Y. Liu, Y. Li. Polythiophene derivative with Phenothiazine-Vinylene conjugated side chain: Synthesis and its application in field-effect transistors, *Macromolecules*, **2007**, 40(20), 7231-7237.
 39. F. Wang, M. Li, B. Wang, J. Zhang, Y. Cheng, L. Liu, F. Lv, S. Wang. Synthesis and characterization of water-soluble polythiophene derivatives for cell imaging, *Sci. Rep.*, **2015**, 5, 7617, 8 pages.
 40. J. Castrellon-Urbe, M. Güizado-Rodríguez, R. Espíndola-Rivera. Photoluminescence analysis of a polythiophene derivative: Concentration and temperature effects, *Opt. Mater.*, **2016**, 58, 93-101.
 41. F. Garnier. Thin film transistors based on molecular semiconductors, *Pure Appl. Chem.*, **1996**, 68(7), 1455-1462.
 42. N. Hebestreit, J. Hofmann, U. Rammelt, W. Plieth. Physical and electrochemical characterization of nanocomposites formed from polythiophene and titaniumdioxide, *Electrochim. Acta.*, **2003**, 48(13), 1779-1788.
 43. J. Obrzut, K. A. Page. Electrical conductivity and relaxation in poly(3-hexylthiophene), *Phys. Rev. B: Condens. Matter Mater. Phys.*, **2009**, 80(19), 195211.

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