

Fluorescent properties of some polythiophenes synthesized from 2-(thiophen-3-yl)acetohydrazide and acetophenone

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Received June 18, 2020; Accepted July 28, 2020

Abstract

In this study, new polythiophenes containing hydrazone groups from derivatives of acetophenone were synthesized by chemical oxidative coupling polymerization. Ultraviolet-visible spectroscopy (UV-Vis) combined with infrared (IR) analyses proved the supposed structure of novel polythiophenes and proved conformance of the expected synthetic method. Morphology and surface properties of the synthesized polymers were investigated by field-emission scanning electron microscopy (FE-SEM). Thermal gravimetry analysis (TGA) has been reported that there was still the presence of small FeCl₃ catalyst in polymers and polymers had a stable thermal stability under air atmosphere. The polymers displayed fluorescence emissions at about 590 nm attributed to the π -conjugated polythiophene. Polymers without doping have a good electrical conductivity (around 4.03×10^{-7} S/cm at 1 MHz).

Keywords. Polythiophenes, chemical polymerization, conducting polymer, fluorescent properties.

1. INTRODUCTION

The synthesis, characterization and physicochemical of polymers have been commonly researched thanks to the ability in complex applications of ionic, electronic conductivity and optoelectronic characteristics.^[1,2] Polythiophene derivatives are of special importance among polymers owing to an exclusive association of high environmental sustainability, structural flexibility of structure, electrochemical, optical and magnetic electrochemical properties.^[3] A lot of works have

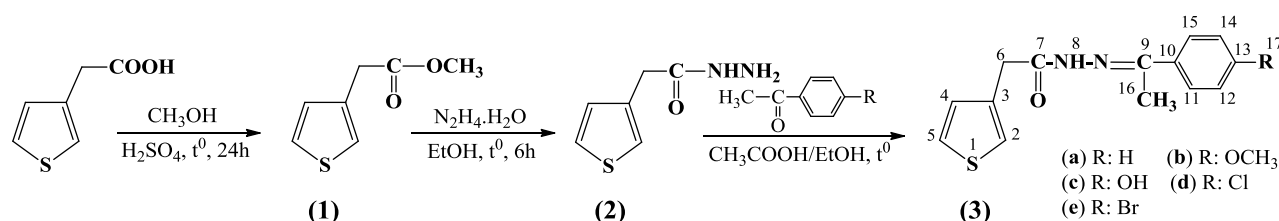
been done on polythiophenes containing long alkyl- or alkoxy- sidegroups as functional substances, for example, organic field-effect transistors (OFETs),^[4,5] organic lightemitting diodes (OLEDs),^[6,7] organic photovoltaic (OPV) cells,^[8,9] and other optoelectronic mechanisms.^[10,11] Polythiophene derivatives all exhibit significant optical features, for instance, thermochromism,^[12] photochromism^[13] and biochromism.^[14] A further application area of polythiophenes is the finding of small bioanalyses, DNA, proteins, metal ions,... using water-soluble sensing sensors.^[15-19]

At first, polythiophene was not studied commonly because of its medium electrical conductivity, as well as its low solubility in water-miscible solvents. However, these disadvantages can be improved by attaching alkoxy or alkyl groups thiophene ring to the 3-position, for example, poly(3- and 3,4-alkylthiophene)s, poly(3- and 3,4-alkoxythiophene)s,...^[20-21] In addition, the length of alkyl side chains also can effect on structure, electrochemical and optical characteristics of polythiophenes.^[22-26] As a result, it is very interesting to prepare polymers from thiophene monomers having long side groups.^[27]

Herein, we present the synthesis and fluorescent properties of a new progression of polythiophenes from 2-(thiophen-3-yl)acetohydrazide and acetophenone. The morphology, thermal stability, optical and conductivity features of the obtained polythiophenes were studied not only on various techniques, but also their capable characteristics and their various functions.

2. MATERIALS AND METHODS

2.1. Synthesis



Scheme 1: Synthesis of monomers **3a-e**

Table 1: The resonant signals to the ¹H-NMR spectra of monomers **3a-e** (ppm)

Proton	3a	3b	3c	3d	3e
H2	7.20 <i>m</i>	7.20 <i>m</i>	7.27/7.30 <i>m</i>	7.28/7.31 <i>m</i>	7.19 <i>m</i>
H4	7.11 <i>dd</i> $J_{2-4} = 1.0, J_{5-4} = 5.0$	7.10 <i>dd</i> $J_{5-4} = 5.0$	7.03/7.07 <i>d</i> $J_{5-4} = 5.0/4.5$	7.03/7.08 <i>d</i> $J_{5-4} = 5.0$	7.08 <i>m</i>
H5	7.26 <i>dd</i> $J_{2-5} = 3.0, J_{4-5} = 5.0$	7.26 <i>m</i> $J_{2-5} = 3.0$	7.43/7.47 <i>dd</i> $J_{2-5} = 3.0, J_{4-5} = 5.0$	7.44 <i>dd</i> $J_{2-5} = 3.0, J_{4-5} = 5.0$	7.27 <i>dd</i> $J_{2-5} = 3.0, J_{4-5} = 5.0$
H6	4.15 <i>s</i>	4.14 <i>s</i>	3.65/3.99 <i>s</i>	3.69/4.03 <i>s</i>	4.13 <i>s</i>
H8	8.90 <i>s</i>	8.73 <i>s</i>	9.69 <i>s</i>	10.54/10.59 <i>s</i>	8.74 <i>s</i>
H11, H15	7.74-7.76 <i>m</i>	7.71 <i>d</i> $J = 9.0$	7.63 <i>d</i> $J = 8.5$	7.81 <i>d</i> $J = 8.5$	7.61 <i>d</i> $J = 8.5$
H12, H14	7.38-7.42 <i>m</i>	6.92 <i>d</i> $J = 9.0$	7.76 <i>d</i> $J = 8.5$	7.46 <i>d</i> $J = 8.0$	7.53 <i>d</i> $J = 9.0$
H16	2.22 <i>s</i>	2.18 <i>s</i>	2.18/2.21 <i>s</i>	2.24/2.27 <i>s</i>	2.19 <i>s</i>
H17	-	3.84 <i>s</i>	10.34 <i>s</i>	-	-

2.1.1. Synthesis of monomers from 2-(thiophen-3-yl)acetohydrazide and acetophenone **3a-e**

The synthesis of methyl 2-(thiophen-3-yl)acetate **1**, and 2-(thiophen-3-yl)acetohydrazide **2**, were reported in our previous study.^[27]

- Synthesis of monomers from 2-(thiophen-3-yl)acetohydrazide and acetophenone **3a-e**

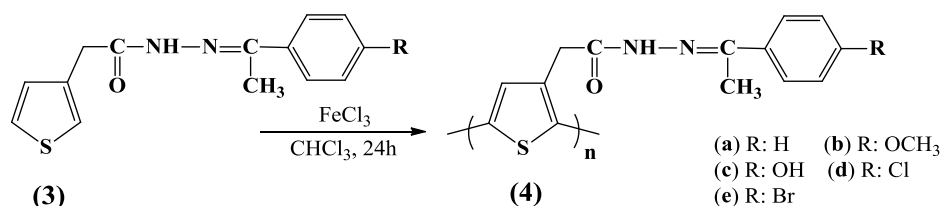
The amounts of **2** (3 mmol) and an appropriate aromatic acetophenone (4.5 mmol) with acid acetic (1.8 mL) were refluxed in ethanol (30 mL) for 6 h. The obtained mixture was kept at room temperature. The precipitates were filtered and recrystallized from ethanol to get monomers **3a-e** (yield 60 % to 75 %) in the shape of crystals with color from white to milky-white; m.p. 163 °C to 200 °C.

The morphology, molecular formula, molecular mass, melting point and IR spectroscopy data of five monomers have been presented in our thesis.^[44] Especially, crystal and molecular structures of two monomers **3b**, **3c** were summarized using X-ray diffraction (XRD).^[40]

Table 2: The resonant signals to the ^{13}C -NMR spectra of monomers **3a-e** (ppm)

Carbon	3a	3c	3d	3e
C2	122.8	122.3/122.4	122.4/122.5	122.8
C3	134.5	135.5/135.8	135.3/135.5	134.4
C4	128.8	128.9/129.0	128.7/128.9	128.7
C5	125.4	125.4/125.6	125.5/125.7	125.4
C6	34.3	34.0/35.7	34.0/35.6	34.4
C7	173.2	166.3/172.4	166.6/172.7	173.5
C9	147.3	152.2	146.0/152.2	146.4
C10	137.9	127.5	133.6/133.8	136.8
C11, C15	125.4	127.4/127.8	127.7/128.0	127.6
C12, C14	128.5	115.9/115.1	128.2/128.3	131.6
C13	129.4	158.4/158.6	136.9	123.7
C16	12.7	13.3/13.9	13.4/13.9	12.7

2.1.2. Synthesis of polythiophenes from 2-(thiophen-3-yl)acetohydrazide and acetophenone **4a-e**

Scheme 2: Synthesis of polythiophene derivatives **4a-e**

Polymers **4a-e** were synthesized from monomers **3a-e** by using anhydrous FeCl_3 as an oxidation substance in dry chloroform to normally get irregular polythiophenes.^[28,29] Under a nitrogen atmosphere, FeCl_3 (4 mmol) was allowed to stir in chloroform (30 mL) for 20 minutes. The mixture of monomers **3a-e** (1 mmol) and chloroform (30 mL) was subsequently gotten ready and dropped gradually to the solution having FeCl_3 . After that, the polymerization reaction was allowed to proceed for an additional 48h under the same condition. After filtering the solution, the black solid was washed with methanol many times and then with distilled water.

A Soxhlet extraction was applied to purify polymers using 300 mL of methanol/ethanol (14:1 v/v) to eliminate the residue remain of FeCl_3 , oligomers and monomers. Lastly, polythiophenes were dried in vacuum for at least 36 h to give from orange to dark red-colored powder of the polymers.

2.2. Devices and Methods

The starting materials were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (United

States). The determination of melting points was carried out on a Gallenkamp melting-point apparatus in the opening in a capillary tube. Infrared spectra of samples were obtained on a Nicolet-Impact 410 FT-IR spectrometer. The polymers were pressed with KBr to form a pellet. The NMR spectra of samples were measured on a Bruker XL-500 spectrometer (USA) using a solvent of $\text{DMSO}-d_6$. Peak multiplicities are reported as s (singlet), d (doublet) and m (multiplet). TG/DTA analysis was recorded on a DTG-60/60H (Shimadzu) between 30 to 600 °C in air at a heating rate of 10 °C/min. The Agilent E4980A Precision LCR meter (United States) was used to determine the conductivity with the polymer tablets of 0.5 cm diameter.

3. RESULTS AND DISCUSSION

3.1. Reaction yield and solubility of polythiophenes synthesized from 2-(thiophen-3-yl)acetohydrazide and acetophenone **4a-e**

Table 3 reports the reaction yield and solubility of polythiophenes from derivatives of acetophenone **4a-e**. It can be seen that the yield of polymerization

reached 59-71 %. All obtained polymers can dissolve slightly in DMSO and CH₂Cl₂. Polymers **4a** and **4e** are slightly soluble in CHCl₃ while only polymer **4e** can dissolve slightly in THF.

3.2. Structure of polythiophenes synthesized from 2-(thiophen-3-yl)acetohydrazide and acetophenone **4a-e**

Structure of conjugated polythiophenes has been elucidated by infrared and UV-Vis spectra. These polymers are slightly soluble in common solutions, therefore, ¹H-NMR are not used to determine the structure of polymers.

3.2.1. FT-IR spectroscopy of polymers **4a-e**

A comparison between monomers **3a-e** and corresponding polymers **4a-e** about the progression of the vibrational frequency showed that the

absorption bands of these polythiophenes were clearly extended compared with the corresponding monomers, related to those of other polythiophenes researched before.^[30,31] In general, it is caused by the wide chain distribution of oligomers and polymers.

Through a comparison between the IR spectrum of monomers and corresponding synthesized polymers, the formation of polythiophene chain was determined. For example, for polymer **4d** (figure 1): There was still a typical band of the N–H bond at about 3437 cm⁻¹ wider than the monomer **3d** caused by intramolecular hydrogen bonds in the polymer. Furthermore, a decline at more than 3000 cm⁻¹ band intensity indicated the transition from C–H thiophene bonds of the monomers to C–C bonds in the polymer chain. In addition, there were clearly the vibrations at 834 cm⁻¹ attributed to out-of-plane C–H bending in the 2,3,5-substituted thiophene ring. This showed that the appearance of polymerization was coupled at the 2- and 5-positions in one thiophene ring.

Table 3: Polythiophene from derivatives of acetophenone **4a-e**

Polymer	Yield, %	Appearance	Solubility			
			DMSO	CH ₂ Cl ₂	CHCl ₃	THF
4a	63	Powder, dark brown	Slightly	Slightly	Slightly	No
4b	61	Powder, dark red	Slightly	Slightly	No	No
4c	71	Powder, dark red	Slightly	Slightly	No	No
4d	59	Powder, dark red	Slightly	Slightly	No	No
4e	68	Powder, red orange	Slightly	Slightly	Slightly	Slightly

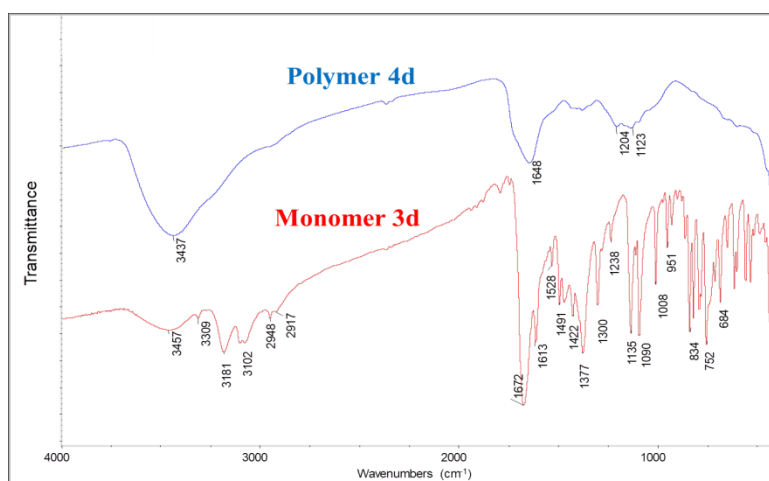


Figure 1: IR spectra of monomer **3d** and polythiophene derivative **4d**

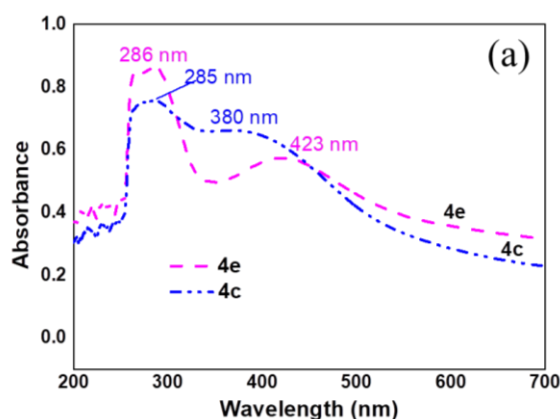
Table 4: Some major vibrations in IR spectroscopy (cm⁻¹) of polymers **4a-e**^[39]

Polymer	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}, \nu_{\text{C=C}}$	$\nu_{\text{C-H out-of-plane}}$
4a	3442.0	1662.4	- , 1540.5	-
4b	3435.6	1664.0	- , 1527.8	834.7
4c	3434.5	1650.7	- , 1519.9	829.6
4d	3437.9	1647.3	1613.1, 1528.6	834.2
4e	3444.5	1668.7	- , 1528.3	829.4

The IR spectra of all polymers show the presence of the strong stretching vibrations of C=O bonds at about 1640-1670 cm^{-1} . There are the shifts of the absorptions with weak-to-moderate intensity of C=N and C=C bonds. However, the stretching bands were partially obscured due to strong stretching bands of C=O groups. A wide and broad band in the 3500-3200 cm^{-1} were attributed to intermolecular hydrogen bonds. The region at about 3100-2800 cm^{-1} showed the occurrence of C-H groups; however, the stretching bands were not clear caused by strong stretching bands of N-H groups.

3.2.2. UV-Vis spectroscopy of polymers 4a-e

The UV-Vis spectra of two DMSO-soluble polymers 4c, 4e are presented in figure 2a. The absorption spectra of both polymer solutions exhibited the absorption bands in 250-550 nm with two maximum absorption bands in the near ultraviolet and visible region. The first absorption band at about 285-286



nm corresponded to $n \rightarrow \pi^*$ transition, which assumes a conformationally semi-twisted polythiophene backbone^[32] or benzene units.^[33] The second absorption band in the longer wavelength (380 and 423 nm) is featured to the energies of $\pi \rightarrow \pi^*$ transition in the π -conjugated polythiophene. Moreover, the λ_{max} of 4e was red shifted by 43 nm related to that of 4c recommending better conjugated level of benzyl substitution.

The UV-Vis spectra of all polythiophenes in solid (figure 2b) displays an absorption band at about 416-466 nm, suitable for $\pi \rightarrow \pi^*$ transition of the π -conjugated polythiophene. In particular, λ_{max} ($\pi \rightarrow \pi^*$) of polymers in solid had a longer wavelength than that in solution. This can be explained by the interchain π - π stacking interactions^[34] or the combination of the directional movements of π -electrons and the increase in vibrations of crystal lattice in solid state.^[35] In addition, the bands characterized for the $n \rightarrow \pi^*$ transition at above 300 nm were partially obscured.

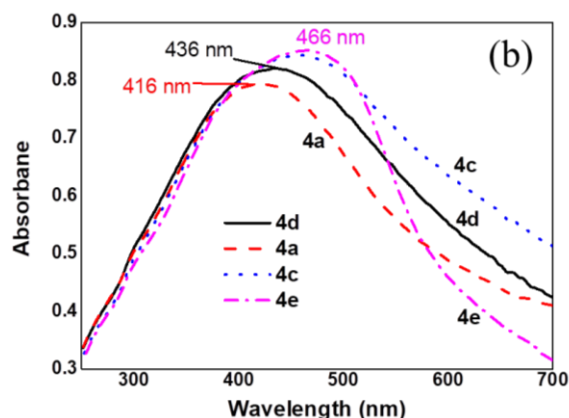


Figure 2: UV-Vis spectra of polymers in DMSO (a) and in solid state (b)

Table 5: The absorption bands in UV-Vis spectra of polymers 4a-e, λ_{max} (nm)/ $\log \xi$

Polymer	Solution in DMSO		Solid
	Absorption band I	Absorption band II	
4a	-	-	416/0.7943
4c	285/0.7545	380/0.6594	458/0.8438
4d	-	-	435/0.8211
4e	286/0.8688	423/0.5736	466/0.8516

3.3. Morphology and properties of polythiophenes synthesized from 2-(thiophen-3-yl)acetohydrazide and acetophenone 4a-e

3.3.1. Morphology of polymers 4a-e

Figure 3 shows the morphology of synthesized polymers 4a-e. With all polymers, the morphology was amorphous indicating clearly the regioirregular polymer synthesized by the chemical oxidation polymerization. It should be noted that the morphological structure of four polymers 4a, 4b, 4d, 4e were porous, inhomogeneous and uniform distribution; whereas particles of polymer 4c showed a tight arrangement with higher adhesion.

3.3.2. TGA of polymers 4a-e

The TG diagrams and thermal properties of polymers 4a-e are presented in figure 4 and table 6. From these results, we can notice that:

Firstly, the all polymers had average thermal stability in the atmosphere at about 420-520 $^{\circ}\text{C}$ (except for 4d). Compared to our previous research,

these polymers **4a-e** had a lower thermal stability than polythiophenes synthesized from benzaldehyde derivatives.^[36] This may be explained by the presence of $-\text{CH}_3$ group in acetophenone leading to the increase in the spatial arrangement in the polymer side chains, resulting in reducing the effective π -conjugated polythiophene and thermal stability.

Secondly, the thermograms exhibited that all polymers were thermally stable above 200 °C and

had drastic degradation above 240 °C. This could be appropriate for the rigidity of polymer backbone when having a long *N*-substituted aromatic side chain.

Thirdly, polymer **4c** had the best thermal stability. This can be explained by the fact that $-\text{OH}$ group in benzyl substituted polythiophene increased the ability to form hydrogen bonds between molecules in the polymer chain, thereby suggesting the higher degree of π -conjugation.

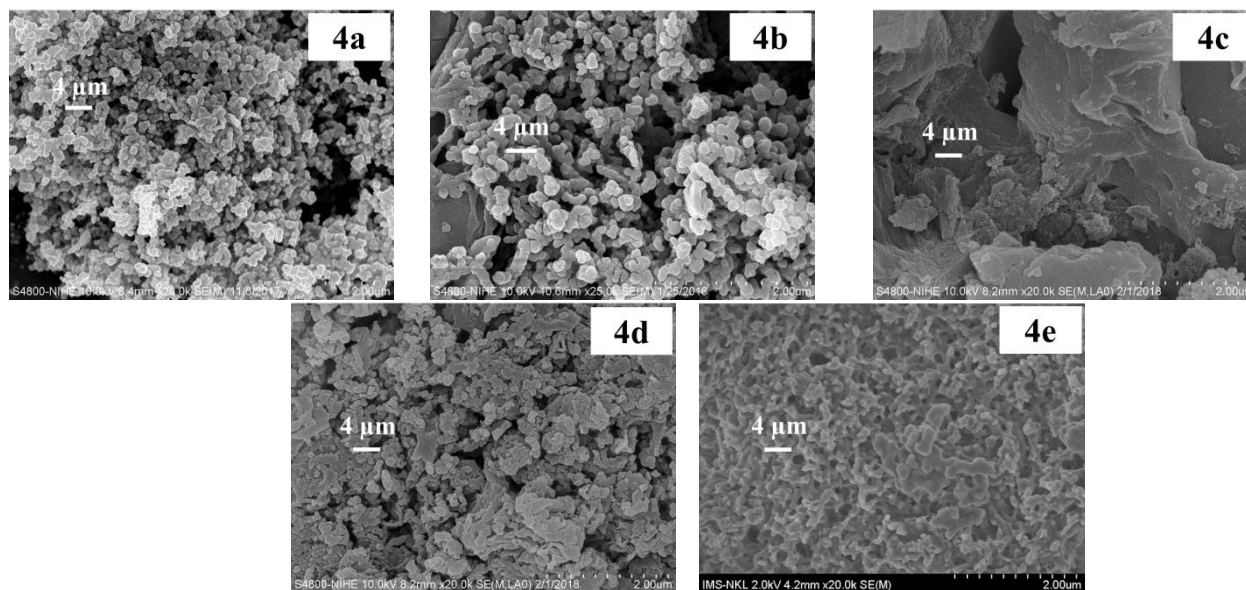


Figure 3: FE-SEM photographs of polymers **4a-e**

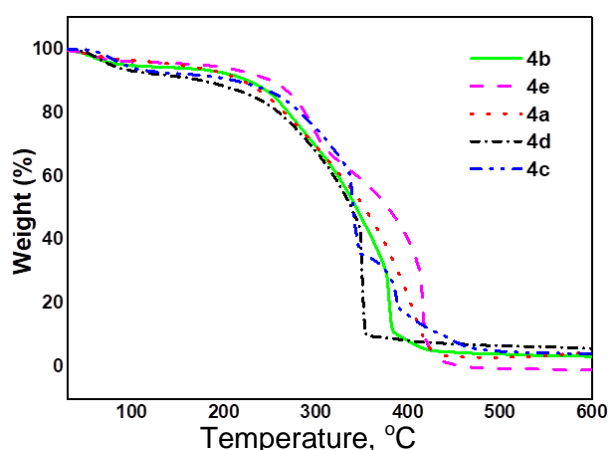


Figure 4: TG curves of polymers **4a-e**

Table 6: Thermal properties of polymers **4a-e**

Polymer	Completely degradation temperature, °C	% W_t Remaining
4a	420	4.59
4b	440	6.10
4c	520	5.31
4d	360	9.84
4e	460	2.06

3.3.3. Photoluminescence spectra of polymers **4a-e**

The analyses of photoluminescence and normalized photoluminescence intensity of four polymers were shown in figure 5. Two polymers **4c**, **4e** had the strongest photoluminescence intensity; polymer **4a** had average photoluminescence intensity and polymer **4d** was not luminescent. These polymers displayed maximum fluorescence emission at about 540 and 590 nm under 415-nm excitation. It is evident that R-substituents in the benzyl moiety have almost no influence on the photoluminescence of the polymers. This difference may be due to the length of the π -conjugated polymer.

Table 7: Emission properties of polymers **4a, 4c-e**

Polymer	$\lambda_{\text{emission}}$, nm	Intensity, a.u
4a	542; 587	10280; 1516
4c	547; 580	23827; 23600
4d	-	-
4e	590	24404

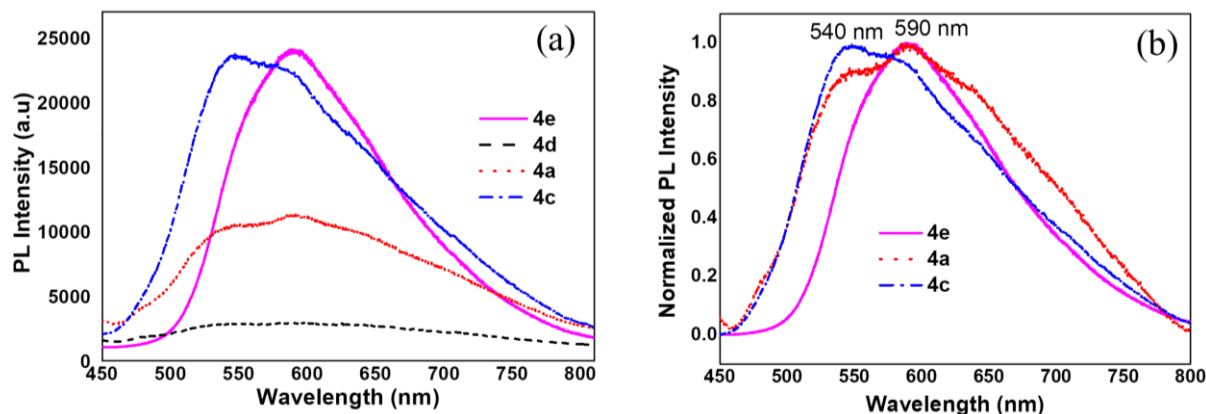


Figure 5: Photoluminescence spectra (a) and normalized photoluminescence intensity (b) of polymers **4a**, **4c–e**

3.3.4. Electrical conductivity of polymers **4a–e**

Electrical conductivity of polymers in the pressed pellets with diameter of 0.5 cm was measured following the increase of frequency from 0 Hz to 1 MHz at 30 °C. The electrical conductivity was increased with the increase in frequency. Polymer **4a** displayed an average conductivity value of 4.03×10^{-7} S/cm at 1 MHz. As can be seen, electron-donating or -withdrawing groups in acetophenone derivatives had an irregular effect on the conductivity of polymers. This is probably due to the position of these groups too far away from the conjugated main chain.

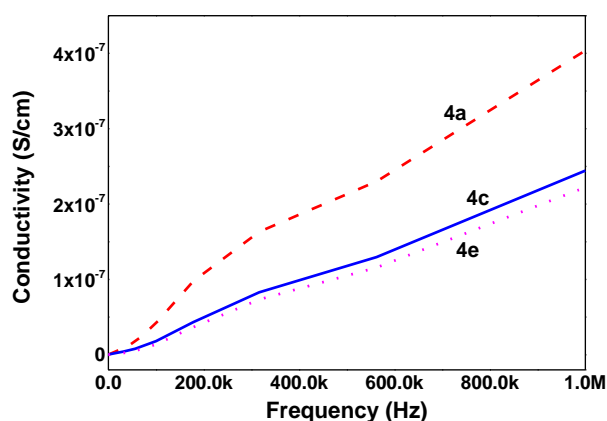


Figure 6: Electrical conductivity of polymer **4a**, **4c** and **4e**

In comparison with polythiophenes synthesized from derivatives of benzaldehyde in our previous study, the conductivity of polymers synthesized from derivatives of acetophenone (**4a**, **4c** and **4e**) was not significantly different.^[36] However, compared with undoped polythiophene with the conductivity between 10^{-7} and 10^{-6} S/cm,^[37] and undoped *p*-type semiconductor poly(3-

hexylthiophene) with moderately low conductivity ($\sim 10^{-8}$ S/cm) in the Hz frequency range of concentration on the majority of electronic functions,^[38] the conductivity of synthesized polythiophene had about 10 times higher. It could be noticed that polythiophenes synthesized from acetophenone derivatives (especially **4a**) have a moderately good electrical conductivity.

4. CONCLUSIONS

In this work, a novel series of polythiophenes containing hydrazone groups from 2-(thiophen-3-yl)acetohydrazide and acetophenone was polymerized by oxidative coupling using anhydrous FeCl_3 in dry CHCl_3 to obtain irregioregular polythiophenes in general. However, properties of these polymers were improved by the long alkyl side chain attached to polymer. Ultraviolet-visible (UV-Vis) spectroscopy combined with infrared (IR) analyses proved the success of the polymerization reaction. Thermal gravimetry analysis indicated that polymers had medium thermal stability in the atmosphere at about 420–520 °C. The maximum fluorescence emission of these polymers was at about 540 and 590 nm; and polymers in the undoped state had a high-quality electrical conductivity, which can be applied for fluorescent dyes or transport materials.

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