

Synthesis and characterization of polythiophenes from hydrazone derivatives sidegroups

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Abstract

Polythiophenes with various substituted hydrazone side groups were synthesized using a chemical oxidative coupling reaction. Analyses of IR and NMR spectra confirmed the expected structure of new synthesized polymers and confirmed suitability of the suggested synthetic route. Surface properties, morphology and thermal stability of the prepared polymers were studied by SEM and TGA methods. Two derivatives were found to have a good solubility in several water-miscible solvents. They can be used as active materials in electrochromic and electronic devices.

Keywords. Polythiophene, hydrazone, chemical polymerization, conducting polymer.

1. INTRODUCTION

Conjugated polyelectrolytes (CPEs) with hydrophobic π -conjugated backbones and hydrophilic ionic side groups show unique optical and electrical properties together with a good solubility in water and water-miscible solvents, making processing of these polymers from aqueous and other environmental friendly solutions possible [1, 2]. As CPEs exhibit both electronic and ionic conductivity, they can be used as active materials in the development of electrochromic devices, or they can facilitate the charge carrier injection in various electronic device structures, such as organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) [3]. The observed performance improvement was ascribed to the redistribution of ions in the CPE film, causing hole accumulation at the interface between the CPE and the active semiconducting polymer [4, 5]. CPEs were also applied to organic photovoltaics for an interfacial electrode engineering [6, 7] and also as new solid polyelectrolytes with increased room-temperature electrical conductivity [8, 9]. Another possible application field of CPEs is their use as water-soluble sensing agents for the detection of DNA, proteins, small bioanalytes, metal ions, and surfactants. The working principles of these sensors are based on changes of UV-Vis and photoluminescence spectra induced by conformational changes of CPE macromolecules

caused by their complexation with oppositely charged analyte species [10-18].

During the last two decades, water-soluble polythiophenes (PTs) and their derivatives are of special importance among CPEs owing to a unique combination of high conductivity, environmental stability, and structural versatility allowing derivatization of the π -conjugated backbone in view of numerous technological applications. A lot of work in this field has been done on CPEs with polythiophene main chain carrying long alkyl- or alkoxy- sidegroups. A family of thiophenes was developed ranging from the unsubstituted, insoluble and intractable polythiophene towards the soluble poly(3-alkylthiophene)s, poly(3-alkoxythiophene), poly(3,4-dialkoxythiophene) [19-25]. Poly(3-hexylthiophene) (P3HT) is one of the most often used materials among organic semiconducting polymers [26,27]. Attaching electron donating groups, such as alkyl- and alkoxy- groups the bandgap can be narrowed and a heightened solubility and thermal stability of polythiophene can be achieved.

2. EXPERIMENTAL

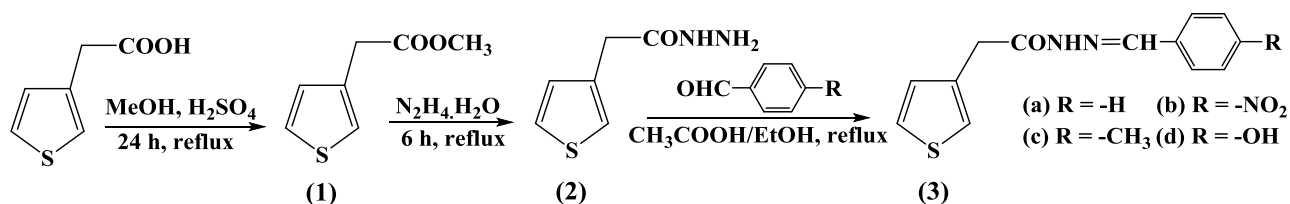
2.1. Synthesis

2.1.1. Synthesis of hydrazones derived from 3-thiophene acetic acid hydrazide **3a-d** [28, 29]

- Synthesis of 3-thiophene methyl acetate (**1**):

3-Thiophene acetic acid (5 mmol) was refluxed in dry methanol (40 mmol) with a small amount of concentrated H_2SO_4 for 24 h. The methanol was evaporated, and the residue was extracted with

diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO_4 and filtered. The resulting residue was recovered after evaporation of the diethyl ether.



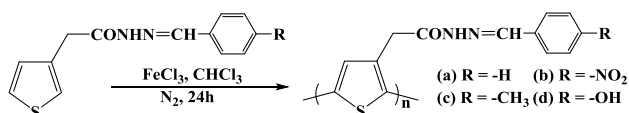
Scheme 1: Synthesis of 3-thienylacetyl hydrazones derived from thiophene-3-acetic acid hydrazide **3a–d**

- Synthesis of thiophene-3-acetic acid hydrazide (**2**): 3-thiophene methyl acetate **1** (5 mmol) was added to excess of hydrazine hydrate (40 mmol) in absolute ethanol (20 mL). The mixture was heated under reflux for 6 h. After cooling the precipitate formed was filtered off, crystallized from ethanol to give hydrazide **2** as white crystals.

- General procedure for synthesis of derivatives of 3-thienylacetyl hydrazones **3a–d**: The amounts of **2** (3 mmol) and an appropriate aromatic aldehyde (6 mmol) with acid acetic (1.5 mL) in ethanol (20 mL) were refluxed for 5 h. The reaction mixture was cooled down and the solid product was separated by filtration and purified by recrystallization in ethanol to give monomers **3a–d**.

2.1.2. Polymerization of derivatives of 3-thienylacetyl hydrazones **4a–d**

The monomers **3a–d** were polymerized by chemical oxidative coupling in dry chloroform using 4 equivalents of anhydrous iron(III) chloride [26, 27]. The polymerization mixture was stirred for 24 h at room temperature under nitrogen atmosphere. The precipitate was filtered, purified by washing with fresh methanol and deionized water several times.



Scheme 2: Polymerization of derivatives of 3-thienylacetyl hydrazones **4a–d**

Polymers **4a**, **4b** and **4c** were purified by Soxhlet extraction with 300 mL of methanol for 48 h to eliminate residual iron(III) chloride and oligomers, and then for 24 hours with 300 mL ethanol to remove monomers. Finally, they were repeatedly

washed with methanol, and vacuum-dried for 2 days to get yield dark red-colored powder of the polymers.

Polymer **4d** was purified by heating it in 2.0 M NaOH aqueous solution at 100 °C for 24 h. After hydrolysis reaction, the mixture was filtered to remove the insoluble part. The water soluble part was neutralized and the solid was precipitated by addition of diluted HCl and collected by filtration. Finally, the reaction mixture **4d** was carefully washed with deionized water repeatedly, and vacuum-dried for 24 h to give dark red-colored powder (70 % yield). Synthesis process is briefly summarized in scheme 2.

2.2. Devices and Methods

All starting materials were purchased from Merck (Darmstadt, Germany) and Sigma–Aldrich (United States), without further purification.

Melting points were measured in open capillary tubes using a Gallenkamp melting point apparatus. The structures of all compounds were confirmed by FT-IR and NMR spectra. IR spectra were recorded using a Nicolet Impact 410 FTIR Spectrometer on KBr pellets of polymer powders mixed with KBr. The $^1\text{H-NMR}$ spectra were recorded on a Bruker XL-500 Spectrometer at 500 MHz using DMSO-d_6 and CDCl_3 as solvents. The data are given in parts per million (ppm) and are referenced to an internal standard of tetramethylsilane (TMS, δ 0.00 ppm). The spin-spin coupling constants (J) are given in Hz. Peak multiplicities are reported as s (singlet), d (doublet) and m (multiplet). The TGA thermograms were recorded 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.

3. RESULTS AND DISCUSSION

3.1. FT-IR spectra

FT-IR spectra of polymers **4a–d** are shown in figure 1. In the IR spectra of ester **1** and hydrazide **2**, the shift of the absorption of the carbonyl group was observed; the vibration frequency of the C=O group of ester **1** at 1735 cm^{-1} is higher than hydrazide **2** at 1687 cm^{-1} . There are shifts of the absorption of the aliphatic C–H group at about $2960\text{--}2850\text{ cm}^{-1}$. However, shifts of the absorption of the C–H bond on the thiophene ring are not observed, since they are obscured by the stretching vibrations in a high frequency region as aliphatic N–H, aliphatic C–H or S–H groups. Additionally, in the IR spectrum of hydrazide **2**, the asymmetric and symmetric stretching vibrations are in a high frequency region (3446 cm^{-1} and 3330 cm^{-1}); and bending vibrations (1620 cm^{-1}) indicate the presence of the N–H bonds in NH_2 group.

In the IR spectra of hydrazones **3a–d**, there are shifts of the absorption of the C=O, C=N and C=C groups at about $1700\text{--}1600\text{ cm}^{-1}$. There are shifts of the absorption of the aliphatic C–H group at about $2950\text{--}2850\text{ cm}^{-1}$.

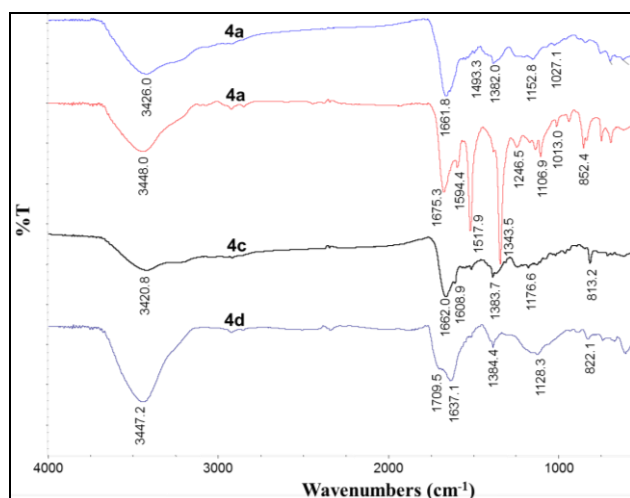


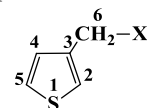
Figure 1: FT-IR spectrum of polymers **4a–d**

The IR spectra of all polymers **4a–d** in figure 1 show the presence of the stretching vibration of C=O, C=N bonds and C=C bonds in a benzene ring at about $1720\text{--}1500\text{ cm}^{-1}$. A strong and wide stretching band in the $3500\text{--}3100\text{ cm}^{-1}$ region is characterized by N–H intermolecular hydrogen bonds, in which, polymer **4d** had the highest frequency region due to the presence of O–H group. The $3100\text{--}2850\text{ cm}^{-1}$ region indicates the presence of C–H group. However, the stretching band was not clear due to a strong stretching bands of N–H and O–H groups.

3.2. NMR spectra

In the $^1\text{H-NMR}$ spectrum of ester **1**, there is a signal of methyl protons (COOCH_3) at 3.62 ppm. Comparison of the $^1\text{H-NMR}$ spectra of **1** with the $^1\text{H-NMR}$ of **2** shows not only the disappearance of the methyl proton signal, but also appearance of additional proton signals of $-\text{CONHNH}_2$ group at 9.14 ppm ($-\text{NH}-$) and 4.19 ppm ($-\text{NH}_2$).

Table 1: The resonant signals to the $^1\text{H-NMR}$ spectra of compounds **1** and **2** (ppm)



X	H2	H4	H5	H6
$-\text{COOCH}_3$	7.32 dd $J = 1,$ $J = 2$	7.03 d $J = 5$	7.47 dd $J = 3,$ $J = 5$	3.69 s
$-\text{CONHNH}_2$	7.22 dd $J = 1,$ $J = 2$	7.01 d $J = 5$	7.43 dd $J = 3,$ $J = 5$	3.36 s

In the $^1\text{H-NMR}$ spectra of monomers **3a–d**, the signals of thiophene and benzene ring protons appear at about 7.04–8.24 ppm. In monomer **3b**, the chemical shifts of the benzene ring protons are larger due to the influence of strongly deactivating group $-\text{NO}_2$. Conversely, for monomer **3d**, the chemical shifts of benzene ring protons attached to strongly activating group $-\text{OH}$ are smaller. The signal of the methylene protons H6 appears in the downfield region at 3.73–4.13 ppm. The results of the analysis of resonant signals of synthesized monomers are summarized in table 2.

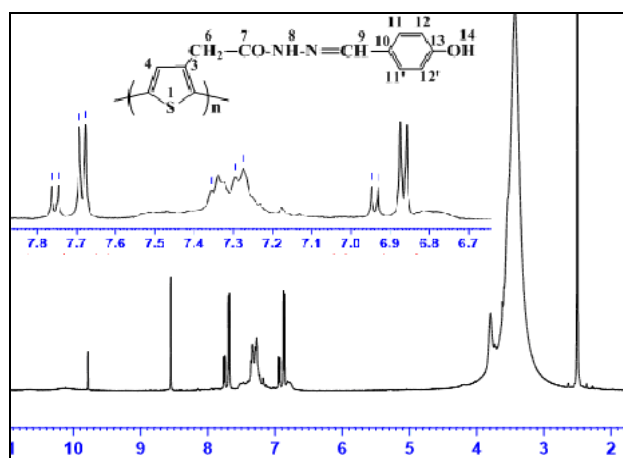


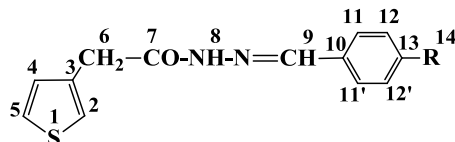
Figure 2: $^1\text{H-NMR}$ spectra of polymer **4d** in DMSO-d_6

$^1\text{H-NMR}$ spectra of polymer **4d** shows similar spectra to the monomer **3d**: benzene ring protons

(about 6.90 ppm and 7.73 ppm), amine proton –NH (9.78 ppm), methine proton =CH (8.55 ppm) and –CH₂ (3.61 ppm). In addition, the signal from proton of the –OH group was not observed. With the

disappearance of the signals from protons of the methine groups (H2 and H5) after the polymerization, thiophene ring proton H4 shows the signal only at about 7.31 ppm.

Table 2: The resonant signals to the ¹H-NMR spectra of monomers **3a–d** (ppm)



Proton	3a	3b	3c	3d
H2	7.22 m	7.19 d $J = 2$	7.22 d $J = 1$	7.19 m
H4	7.12 dd $J = 1, J = 5$	7.10 d $J = 5$	7.12 d $J = 4.5$	7.11 d $J = 3$
H5	7.36 dd $J = 3, J = 5$	7.28 dd $J = 3, J = 5$	7.26 d $J = 3$	7.25 dd $J = 3, J = 5$
H6	4.13 s	4.11 s	4.12 s	4.08 s
H8	9.84 s	11.16 s	9.29 s	9.17 s
H9	7.80 s	8.00 s	7.73 s	7.79 s
H11, H11'	7.67 dd $J = 7.5, J = 2$	7.82 d $J = 9$	7.56 d $J = 8.0$	7.52 d $J = 8.5$
H12, H12'	7.40 m (ov)	8.24 d $J = 8.5$	7.22 d $J = 7.5$	6.87 d $J = 8.5$
H13	7.41 m (ov)	-	-	-
H14	-	-	2.39 s	10.10 s

3.3. SEM analysis

SEM images of thin films of the derivatives under study are shown in figure 3. With all polymers **4a–d**, the morphology is amorphous pointing to a regioirregular structure of the polymer chains synthesized by the chemical oxidation polymerization reaction. In three polymers, **4a**, **4c**, **4d**, densely packed particles of polymer with small dimensions and relatively uniform size distribution are observed. They show more granular structure, better homogenous morphology and higher than polymer **4b**.

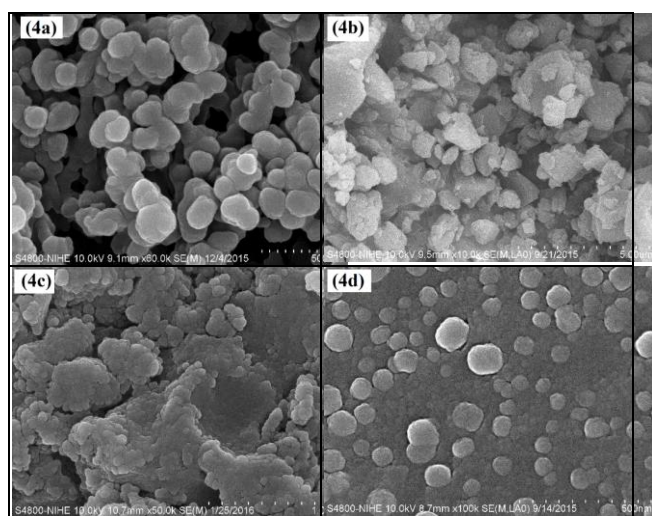


Figure 3: SEM micrographs of polymers **4a–d**

3.4. TGA analysis

The side groups of benzene ring of the phenylhydrazone group play an important role in the polymer thermal stability. Therefore, we performed TGA and DTA analyses of polymers **4a–d** (see figure 4). The TGA curves of three polymers **4a–c** show 100 % weight loss when heated to 600 °C; polymer **4a** has the lowest thermal stability with the weight losses in three clearly distinguished steps. Polymer **4d** has the highest thermal stability and weight losses are gradual with increasing temperature. The remaining weight of polymer **4d** at 600 °C was observed to be very high, up to above

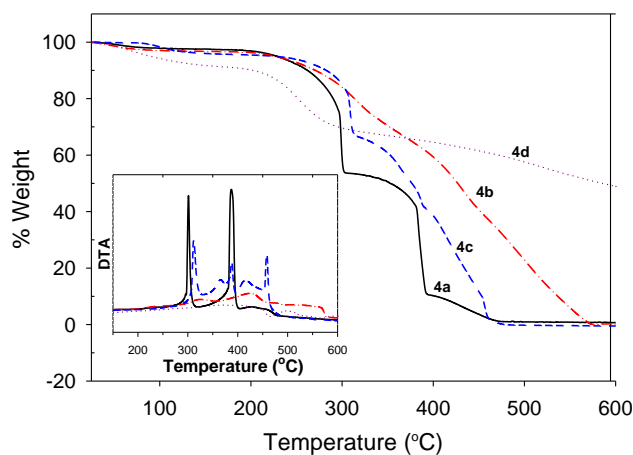


Figure 4: TGA and DTA (inset) thermograms of polymers **4a–d**

40 % compared to the weight of the initial polymer. The difference between the good thermal stability of the polymer **4d** and the medium stability of polymers **4a–c** should be ascribed to hydrogen bond of the –OH group.

4. CONCLUSION

We have successfully synthesized a new class of irregioregular polythiophene with hydrazine derivatives sidegroups using the chemical oxidative coupling reaction. Amorphous morphology affected by the irregular structure of the main polymer chain was confirmed by SEM observations. Based the TGA analysis, these polymers exhibit good stability, especially polymer **4d**, with the remaining weight at 600 °C up to above 40 % compared to the weight of the initial polymer. Two polymers **4b** and **4d** have the good solubility in some water-miscible solvents as dimethyl sulfoxide and dimethylformamide, which can facilitate the preparation of composites of these polymers with noble-metal nanoparticles and other inorganic and organic compounds, and their blends with anionic polyelectrolytes.

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