

On the polymerization reactions of thiophene monomers under atmospheric plasma conditions

T. Teslaru¹, R. Jijie¹, M. Dobromir¹, V. Pohoata¹, I. Topala¹, V. Antoci², C.-I. Ciobanu², N. Dumitrascu¹

¹Iasi Plasma Advanced Research Center (IPARC), Faculty of Physics, Alexandru Ioan Cuza University of Iasi, Blvd. Carol I No. 11, Iasi 700506, Romania

²Research Department, Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, Blvd. Carol I No. 11, Iasi, 700506, Romania

The plasma polymerization reactions of thiophene monomers were performed in a dielectric barrier discharge (DBD) reactor working at atmospheric pressure in helium. The chemical composition of plasma polythiophene film and a possible polymerization mechanism were investigated by Fourier Transform Infrared Spectroscopy, X-ray Photoelectron Spectroscopy and Nuclear Magnetic Resonance Spectroscopy.

1. Introduction

Plasma polymerization is a rapid process which involves complex physico-chemical reactions. In plasma, chemically reactive species, mostly free radicals are created by activation, fragmentation of the monomer molecules and then are randomly recombined into highly branched and crosslinked structure [1, 2]. The final compounds are deposited on any surface in contact with plasma and are conventionally called plasma polymer films [2].

The physico-chemical properties of plasma polymer films, e.g., the surface chemistry, thickness, homogeneity, morphology, conductivity, aqueous stability depend on the chemical composition the monomer and plasma reactor parameters, such as gases composition and its flow rates, geometrical and electrical parameters of discharge [3, 4]. In order to control the plasma polymer films properties it is necessary to study the intermediary reactions during plasma polymerization [4].

Polythiophene (PTh) it is a heterocyclic polymer that has particular interest due to its properties that can be used in various applications, such as solar and photovoltaic cells [5, 6], biosensors, tissue engineering scaffolds [7], antistatic coatings.

Polythiophene has been prepared by several techniques, including chemical and electrochemical polymerization [5, 7], and also vapor deposition techniques such as polymerization under the plasma conditions [3, 8].

The plasma polymerization of thiophene precursors, it is a promising alternative method to obtain polythiophene films. Indeed this solvent-free process presents significant advantages over the wet-chemistry methods such as one-step of processing and fast deposition of film on different types of

substrate, including polymers, metals, glasses, ceramics, Si-wafers.

The goal of this study is to investigate polymerization reactions of thiophene monomer under atmospheric pressure plasma, based on the chemical analysis of the final product.

The Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Photoelectron Spectroscopy (XPS) and Nuclear Magnetic Resonance Spectroscopy (¹H-NMR) were used to investigate the chemical composition of plasma polythiophene (pPTh) film and a possible mechanism of polymerization is proposed.

2. Experimental

2.1. Plasma polymerization set-up

Plasma polymerization reactions of thiophene (Th) monomer were performed in a dielectric barrier discharge (DBD) reactor, as can be seen in Fig. 1.

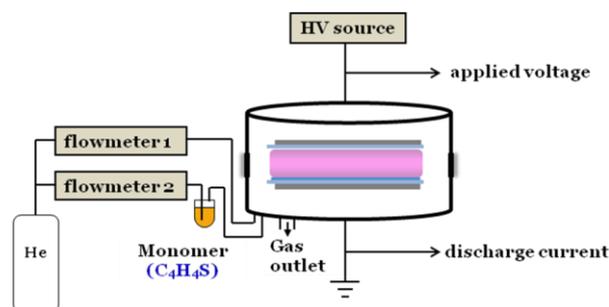


Fig. 1. Experimental set-up of plasma polymerization reactor

The plasma reactor consists of a stainless steel chamber and two plane-parallel electrodes (30 mm in diameter) obtained by deposition of copper onto

glass dielectrics substrates by the use of a magnetron discharge. The gap between electrodes was fixed to 5 mm. The gas flow rates were maintained constantly during plasma polymerization by the use of two flowmeters (MKS type 1179B). Thiophene vapors were introduced in the discharge by gas bubbling. Two gas lines were used to feed the plasma reactor: the working line used to sustain the discharge and the carrier line used to transport Th vapors into the plasma region. The helium and the Th monomer flow rates were fixed to 2.9 l/min and 103 μ l/min (corresponding to 0.1 l/min flow rate of bubbling gas). High voltage pulses were applied on the power electrode using a digital waveform generator (Tabor Electronics, WW5064) and high voltage amplifier (Trek Model PD07016). The wave shape of applied signal was a square type, 6 kV amplitude, 250 μ s width, 2 kHz frequency and 50% duty cycle. The deposition time was 10 min.

2.2. Materials and methods

Thiophene (C_4H_4S , 99.00% purity, $M = 84.14$ g/mol) was purchased from Merck, Germany (Fig. 2a).

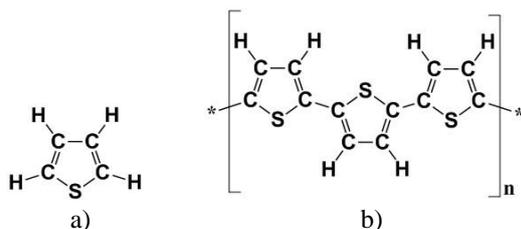


Fig. 2. Chemical structure of a) thiophene; b) polythiophene

Helium with a purity of 98.999% was supplied by Messer Gas SRL, Romania. NaCl plates were used as substrates for the FTIR spectroscopy and glass slides for XPS. Borosilicate tubes (5 mm diameter) were used for NMR spectroscopy, hosting the polymer solution in DMSO-*d*₆ solvent. All substrates were cleaned with ethanol and distilled water at room temperature.

FTIR measurements were performed using a Bomem MB-104 spectrometer in the transmission mode, in the range of 4000 – 400 cm^{-1} .

XPS analyses were achieved using a PHI 5000 VersaProbe spectrometer (Physical Electronics) with a monochromatic Al K_{α} X-ray source ($h\nu = 1486.7$ eV) operating at a power of 25.4 W. The photoelectron take-off angle was 45° relative to the sample surface. During the measurements, the pressure in the analysis chamber was kept at 2×10^{-6} Pa. The energy scale was calibrated by reference to carbon peak C1s at 284.6 eV and resolution of the XPS analyzer is 0.85 eV for organic materials.

The NMR spectra have been recorded on a Bruker Avance III 500 spectrometer, equipped with a 5 mm PABBO detection probe, operating at 500.1 MHz for 1H nucleus. Deuterated dimethylsulfoxide (DMSO-*d*₆) was used as solvent for the pPTh films and monomer Th. In 1H -NMR spectra, chemical shifts are reported in δ units (ppm) relative to the residual peak of solvent (ref: DMSO, 1H : 2.50 ppm).

1H -NMR signals of pPTh film is very weak because a small amount of polymer is dissolved in the solvent used for this analysis.

3. Results and discussions

3.1. FTIR Spectra Analysis

The FTIR spectra of the monomer (Th) and pPTh film are given in Fig. 3.

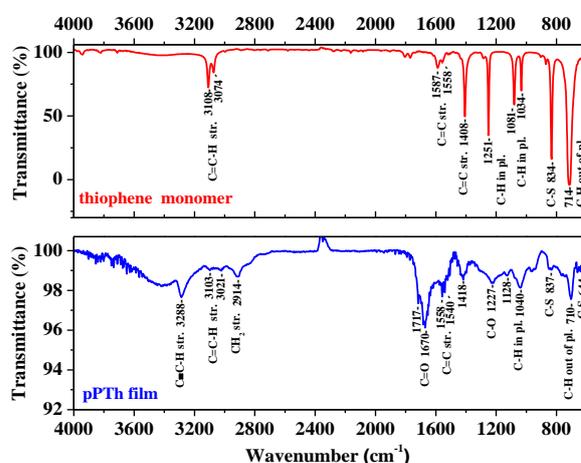


Fig. 3. FTIR spectra of Th monomer and pPTh film

The FT-IR spectrum of pPTh film contains bands that represent carbon-carbon (C-C, C=C), and carbon-sulfur (C-S) bonds characteristic to the Th monomer. Also contains predominant bands that can represent carbon-oxygen (C-O, C=O) bonds.

The FTIR spectrum of polymer contain two small absorption bands at 3021 and 3103 cm^{-1} that can be assigned to the C-H stretching vibration of the Th ring and three absorption bands at 1558, 1540 and 1418 cm^{-1} which are characteristic to the aromatic C=C stretching vibration. Also bands at 1128, 1040 and 710 cm^{-1} related to in-plane and out-of-plane C-H deformation vibration in Th ring as well bands at 644 and 837 cm^{-1} associated to C-S bond. These results confirm the presence of Th ring in the pPTh film structure. In addition certain absorptions bands in the IR region that are not present in the monomer spectrum suggest fragmentation of the monomer structure. Thus aliphatic absorption band is observed at 2919 cm^{-1} corresponding to methylene (CH_2) group, and at 3289 cm^{-1} to specific to acetylenic ($C\equiv C-H$) group. The absorption bands at 1676, 1717

cm^{-1} (C=O stretch) and 1227 cm^{-1} (C-O stretch) confirm the inclusion of small amount of oxygen in the film, results which are in agreement with the XPS data.

3.2. XPS Spectra Analysis

XPS spectrum of the pPTh film indicates the presence of 71.9 % carbon (C1s at 284.6 eV), 19.9 % sulfur (S2p at 163.3 eV) and 8.2 % oxygen (O1s at 531.9 eV).

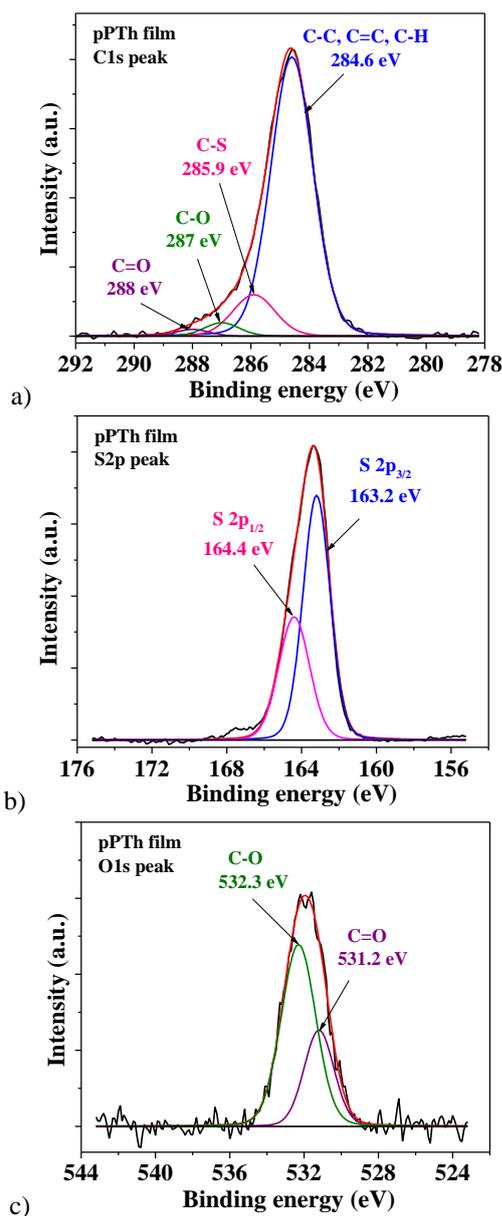


Fig. 4.a) XPS spectra deconvolution of pPTh film
a) C1s; b) S2p and c) O1s

The fitted C1s signal contains four distinctive components (Fig. 4a) attributed to C-C, C=C, C-H bonds (284.6 eV), C-S bond (285.9 eV), C-O bond (287 eV) and C=O bond (288 eV). The S2p signal

(Fig. 4b) was decomposed in two peaks attributed to $\text{S}2\text{p}_{3/2}$ (163.2 eV) and $\text{S}2\text{p}_{1/2}$ (164.4 eV). O1s signal contain two peaks associated with a single bond C-O at 532.3 eV) and a double bond C=O at 531.2 eV (Fig. 4c).

The oxygen can be incorporated in the pPTh matrix during plasma polymerization process because we worked at atmospheric pressure and from reaction with air after the reactor is opened (Table 1).

Table 1. Elemental composition of pPTh film

Chemical composition	%C1s	%S2p	%O1s	C/S	C/O
Theory	80	20	-	4.00	-
pPTh	71.9	19.9	8.2	3.61	8.76

3.3. NMR Spectra Analysis

In order to obtain further information on molecular structure, $^1\text{H-NMR}$ spectra of thiophene monomer and pPTh films were recorded (Fig. 5, Fig.6).

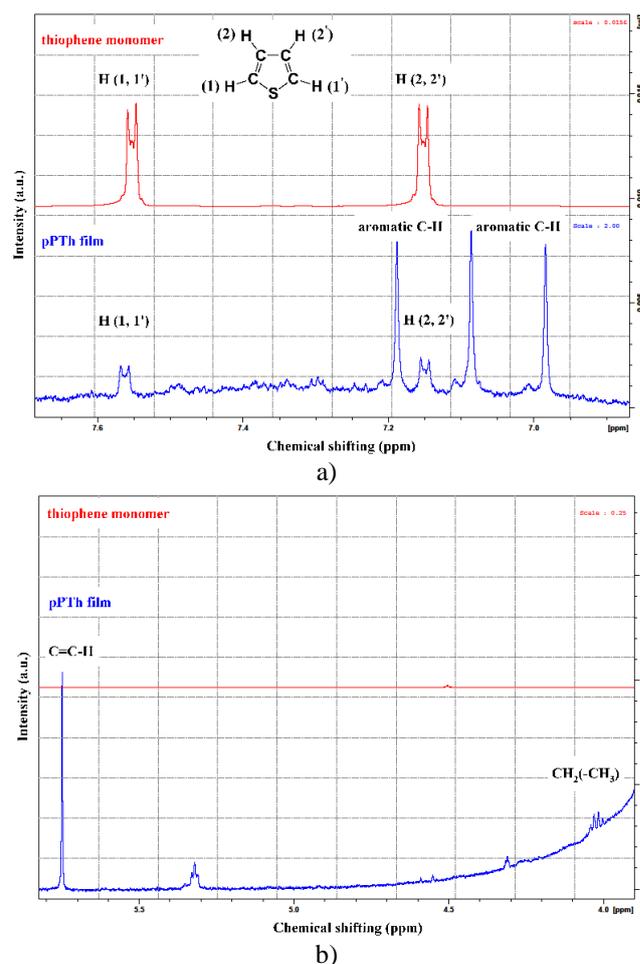


Fig. 5. $^1\text{H-NMR}$ spectra of thiophene monomer and pPTh film: a) aromatic region; b) aliphatic region

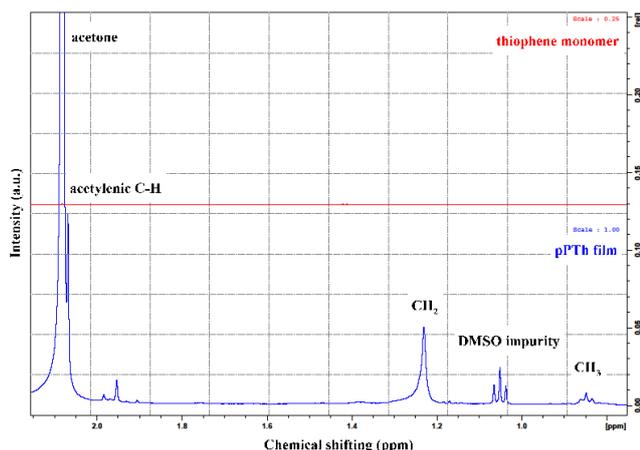


Fig. 6. ¹H-NMR spectra of thiophene monomer and pPTh film (aliphatic region)

¹H-NMR spectrum of thiophene monomer contains two types of signals: a doublet corresponding to equivalent protons H1 and H1' which appears at 7.547–7.559 ppm, and a signal corresponding to the protons H2 and H2', being a doublet at the chemical shifts between 7.146–7.158 ppm.

¹H-NMR spectrum of polythiophene film, obtained at atmospheric pressure plasma, provides two signals corresponding to monomer protons at the chemical shifts between 7.144–7.155 ppm and 7.555–7.569 ppm, respectively. These signals confirm the presence of intact thiophene molecules in pPTh film. Also new signals are observed, these indicating thiophene ring fragmentation. Thus, the signal for methylene group $\text{CH}_2(-\text{CH}_3)$ appears like a quartet at the chemical shifts 4.041–4.003 ppm, and for methyl group $\text{CH}_2(-\text{CH}_3)$ the signal is a triplet at 0.862–0.835 ppm. In addition the ¹H-NMR spectrum of pPTh film shows three singlet signals in the region 7.876–6.984 ppm characteristic of aromatic compounds. In the aliphatic region of the spectrum is present a signal at 2.068 ppm which can be associated with an acetylenic hydrogen ($\text{C}\equiv\text{C}-\text{H}$). A signal that can be attributed to the vinyl protons ($\text{C}=\text{C}-\text{H}$) appears at chemical shift 5.748 ppm. Also at 1.23 ppm appears a singlet that could be attributed to the existence of methylene CH_2 protons in polymer film.

4. Conclusion

A dielectric barrier discharge reactor working under atmospheric pressure conditions has been used to initiate plasma polymerization reactions of thiophene monomer. The pPTh film was characterized by spectroscopic analyses providing it chemical composition and incorporation of oxygen in the final compound. The FTIR and NMR

spectroscopy revealed the thiophene ring was opened, due to electron impact processes and new fragments are formed. Also the ¹H-NMR spectrums confirm the presence of intact thiophene molecules in pPTh matrix a fact that could be due to rapid polymerization process and the pulsed mode of dielectric barrier discharge operation.

5. References

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6. Acknowledgments

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