

# Poly(3-methoxyethoxythiophene) and its Copolymers with Aniline, Thiophene and Pyrrole: Chemical and Electrochemical Synthesis

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## ABSTRACT

We have investigated the chemical and electrochemical polymerization of a thiophene derivative functionalized with a 3-methoxyethoxy moiety and its copolymers with aniline, thiophene and pyrrole. Chemical polymerization of monomers was carried out in presence of  $\text{FeClO}_4 \cdot 9\text{H}_2\text{O}/\text{HClO}_4$  oxidant. The electropolymerization by a cyclic voltammetry method was studied under the sufficient concentrations of monomer, 0.1 M tetrabutylammonium hexafluorophosphate, 20 mL acetonitrile, GC disk working electrode, Ag/AgCl reference electrode and platinum wire counter electrode conditions. The produced films give highly conducting polymeric materials, some of which are soluble in common organic solvents. The conductivity of polymers was measured by four-point probe technique. The undoped state of the polymers possessed conductivities of lower than  $10^{-4}$ – $10^{-3}$  S/cm. After doping with  $\text{FeCl}_3$ / nitromethane or vapour  $\text{I}_2$ , conductivities increased to  $10^{-3}$ – $10^{-2}$  S/cm. Properties of the polymers were characterized using UV, IR, NMR, CV and GPC.

**Key Words:** chemical and electrochemical polymerization, conducting polymers, 3-methoxyethoxythiophene, copolymer

## INTRODUCTION

A significant advance in the study of conducting polymers was made when the synthesis of "soluble"  $\pi$ -conjugated polymers were reported. The first of these soluble polymers were the poly(3-alkylthiophenes) which were obtained by derivatization of the  $\beta$ -position of the thiophene ring with alkane substituents [1]. It

was shown that incorporation of the side groups on conjugated polymer chains increases their processability, but it was anticipated that derivatization of the polymer backbone would affect conductivity by modifying the planarity of the backbone, thus interfering with electron transport along, and between, polymer chains.

Poly(thiophene) compounds have very high

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application prospects due to their high ionization potential and storage stability. To be potentially useful in electronic application, a material must have excellent electronic and mechanical properties and it should be either a solution or a melt processable material with high environmental stability. For this, the substitution on the 3-position of poly(thiophene) could be an interesting alternative route for electrode functionalization [2].

A series of polyalkoxythiophene with chains of different lengths [3] and other molecules with several ether functions and with the first oxygen atom spaced from the thiophene ring by one or two  $\text{CH}_2$  groups [4] have also been prepared. Roncali [5] reported that the polymer obtained from the monomer that contains two  $\text{CH}_2$  groups between the thiophene ring and the first oxygen atom, and with two ether functions, has a greater stability by comparison with the other molecules of the series. Soluble conducting polymers are studied extensively [6] and they have potential applications in various domains: battery, electrocatalytic material, electromagnetic shielding and sensors [7, 8].

Poly(3-alkylsulphonate)thiophenes have recently been claimed to be soluble in water and organic solvents, both in the undoped and doped states [9–11]. We describe the preparation 3-methoxyethoxythiophene. Then, poly(3-MET) and its copolymers with aniline, thiophene and pyrrole prepared by chemical and electrochemical polymerization. Polymers were prepared by chemical and electrochemical oxidation of the monomers using  $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$  and cyclic voltammetry method, respectively. After polymerization of these substituted heterocycles, the polymers showed indeed new properties as fusibility or solubility.

## EXPERIMENTAL

### Instruments and Materials

Conductivity changes were measured with a four-probe device (home-made). A Fourier transform infrared (8101 M-Shimadzu) was used in spectral studies of the films. Vibrational transition frequencies are reported in wavenumber ( $\text{cm}^{-1}$ ). Band intensities are

assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Cyclic voltammetry and electrochemical polymerization were carried out using digital potentiostat DP8 (home-made). Proton nuclear magnetic resonance ( $\text{FT-}^1\text{H NMR}$ ) spectra were recorded at 200 and 400 MHz on a Bruker WP 200 SY spectrometer. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity and integration. Visible spectra were obtained by Perkin Elmer Lambda 15 spectrophotometer.

Molecular weights were measured at 30 °C with a gel permeation chromatography, GPC, (Waters Associates, model 150-C). Three styragel packed columns with different pore sizes ( $10^4$ – $10^6$  Å) were used. The mobile phase was tetrahydrofuran with flow rate of 1.5 mL/min. The solution concentration was 0.2 wt%. Calibration of the instrument was performed with nine standard samples of monodisperse polystyrene having molecular weights between  $3.0 \times 10^3$  and  $1.4 \times 10^6$ . Pyrrole (GPR) and thiophene (Merck) were dried with NaOH, fractionally distilled under reduced pressure from sodium or  $\text{CaH}_2$ . Aniline was purified, after refluxing with 10% acetone for 10 h and aniline was acidified with HCl, then extracted with  $\text{Et}_2\text{O}$  until colourless. The hydrochloride was purified by repeated crystallization before aniline was liberated by addition of alkali, then dried with solid KOH, and distilled under reduced pressure. Acetonitrile and nitromethane (Merck) were dried on silicagel, distilled on phosphoroxide in the presence of nitrogen gas [12]. The ferric perchlorate was prepared by alkali method [13]. All the other materials and gases used in this work were purchased from Merck chemicals and purified, or were prepared by methods in literature.

### Preparation of 3-Methoxyethoxythiophene (3-MET)

The synthesis of the 3-methoxyethoxythiophene was carried out following the method reported by Bryce et al. [12].

### Chemical Polymerization of 3-MET

Chemical polymerization of 3-MET, for obtaining poly(3-MET), was carried out in a conventional reaction vessel. The bottom of the reaction vessel was

covered with 25 ml  $\text{HClO}_4$ , 9.1 M containing an oxidant, such as  $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ . The 3-MET (57 mmol) was dissolved in 15 mL benzene and then floated on the surface of the aqueous solution in the vessel. After 30 min the polymeric film was formed at the interface of the aqueous and organic solutions at  $5^\circ\text{C}$  under a  $\text{N}_2$  atmosphere.

A polymeric film without air exposure was repeatedly washed with methanol at reflux conditions and then dried under vacuum for 2 h. Prepared film was soluble in some of organic solvents such as dimethylformamide, dichloromethane, chloroform and acetonitrile.

UV(acetonitrile);  $\lambda_{\text{max}}=493.8$  nm (1.7 intensity), neutral form and a broad peak 780 nm (0.5 intensity) doped form (brown-red solution). FT-IR (KBr); 3010 (sh), 2994 (w), 1490 (m), 1440 (m), 1310 (m), 1230 (w), 1213 (m), 1085 (m,  $\text{ClO}_4^-$ ), 660 (m)  $\text{cm}^{-1}$ .

FT- $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  6.3 (s, 1H), 4.0 (t, 2H), 3.5 (t, 2H), 3.4 (s, 3H) ppm.

#### Chemical Copolymerization; General Procedure

Chemical copolymerization of 3-MET (1 mmol) and monomers (aniline, thiophene or pyrrole) (1 mmol) carried out by a conventional reaction in the 25 mL methanol solution containing  $\text{FeClO}_4 \cdot 9\text{H}_2\text{O}$  (4 mmol). Copolymeric material was precipitated in the bottom of reaction vessel at  $5^\circ\text{C}$  under a  $\text{N}_2$  atmosphere after 45 min. Copolymers were filtered and were repeatedly washed with methanol and then dried under vacuum for 4 h. These copolymers were soluble in some of the organic solvents such as dimethylformamide, dichloromethane, chloroform and acetonitrile, the same as poly(3-MET).

#### Poly(3-methoxyethoxythiophene-co-aniline),

##### Poly(3-MET-co-ANI)

UV (acetonitrile);  $\lambda_{\text{max}}=340.1$  nm (1.8 intensity), 440.2 nm (0.65 intensity), 645.1 nm (0.65 intensity), neutral form and a broad peak 890 nm (1.7 intensity), doped form (blue-green solution). FT-IR (KBr); 3746 (br), 3229 (w), 2920 (m), 1574 (m), 1501 (m), 1312 (m), 1286 (m), 1283 (m), 1246 (w), 1142 (s), 1102 (m,  $\text{ClO}_4^-$ ), 814 (s), 617 (s), 509 (m)  $\text{cm}^{-1}$ .

FT- $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  8.1 (s, 1H), 6.9 (d, 4H),

6.1 (s, 1H), 4.2 (t, 2H), 3.8 (t, 2H), 3.4 (s, 3H) ppm.

#### Poly(3-methoxyethoxythiophene-co-thiophene),

##### Poly(3-MET-co-Th)

UV (acetonitrile);  $\lambda_{\text{max}}=500$  nm (0.35 intensity), neutral form and a broad peak 880 nm (1.35 intensity) doped form (blue solution). FT-IR (KBr); 3050 (m), 2990 (w), 1500 (m), 1460 (m), 1400 (m), 1250 (m), 1220 (s), 1090 (m,  $\text{ClO}_4^-$ ), 821 (s), 719 (m)  $\text{cm}^{-1}$ .

FT- $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  6.2–7.1 (m, 3H), 4.1 (t, 2H), 3.7 (t, 2H), 3.4 (s, 3H) ppm.

#### Poly(3-methoxyethoxythiophene-co-pyrrole),

##### Poly(3-MET-co-Py)

UV (acetonitrile);  $\lambda_{\text{max}}=361.6$  nm (0.23 intensity), 530 nm (0.52 intensity), neutral form and a broad absorption 840.2 nm (2.1 intensity), doped form (violet solution). FT-IR (KBr); 3350 (s), 3010 (m), 2990 (m), 1510 (m), 1460 (m), 1400 (m), 1320 (m), 1276 (m), 1269 (m), 1176 (s), 1099 (m,  $\text{ClO}_4^-$ ), 990 (s), 914 (sh), 790 (m)  $\text{cm}^{-1}$ .

FT- $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  8.2 (s, broad, 1H), 6.3 (d, 2H), 6.2 (s, 1H), 4.3 (t, 2H), 3.9 (t, 2H), 3.5 (s, 3H) ppm.

#### Films Preparation

One gram of poly(3-MET), poly(3-MET-co-ANI), and poly(3-MET-co-Th) or poly(3-MET-co-Py) powder was slowly added (over 1 h) to 40 mL of dimethylformamide (DMF) solution, and magnetically stirred at room temperature for 7 h. The resulting viscous solution was pre-filtered twice through a Buchner funnel using Whatman paper #541 to remove large particles. Finally it was filtered with Whatman paper #542. The produced viscous solution of polymer and copolymers were spread over a piece of glass to obtain an even layer of films. These were then dried under vacuum. In general slower drying gave films with more uniform thickness. Dried films were removed from the glass by immersion in water. The films were prepared from 6 mL of solution cast over a piece of glass (8×8 cm) gave a film with thickness of  $\approx 20$ –30  $\mu\text{m}$ .

#### Electrochemical Polymerization

All electrochemical polymerizations of 3-MET and its

copolymerizations with aniline, thiophene and pyrrole were performed using a conventional three-electrode system with a Ag/AgCl reference electrode ( $0.01 \text{ mol L}^{-1}$ ), platinum wire counter electrode and GC disk working electrode. All solutions for electrochemical polymerization were freshly prepared using nitrobenzene distilled from calcium hydride and stored over molecular sieves. Tetrabutylammonium hexafluorophosphate (Aldrich) was bubbling dry oxygen free nitrogen for at least 20 min before each polymerization. Polymers were grown on GC disk electrode under scan potential in the range of 500–1800 mV and scan rate 50 mV/s. The thickness of the film was ca.  $0.5 \mu\text{m}$  as determined by scanning electron microscopy.

## RESULTS AND DISCUSSION

As it has been pointed out in the first part of this study the poly(3-MET) is soluble in organic solvents, but it is not very stable. So, we tried to copolymerize it with aniline, thiophene and pyrrole by using chemical and electrochemical methods. The constant potential copolymerizations were performed in the same electrolyte as before with monomer concentration of 0.03 M for the 3-methoxyethoxythiophene and 0.03 M for the aniline, thiophene and pyrrole. The black films were formed on the anode and they

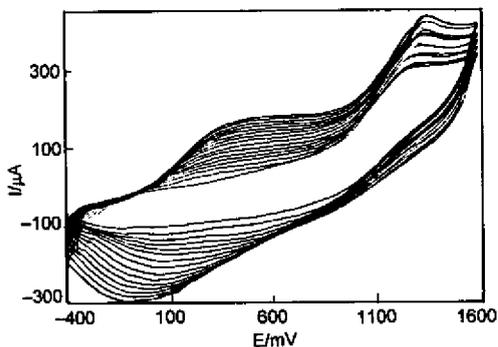


Figure 1. Cyclic voltammograms of 3-MET 1 mM-aniline 1 mM mixture in  $\text{PhNO}_2$ ,  $0.1 \text{ Bu}_4\text{NPF}_6$ , GC disk electrode vs. Ag/AgCl, scan rate=50 mV/s (15 cycles).

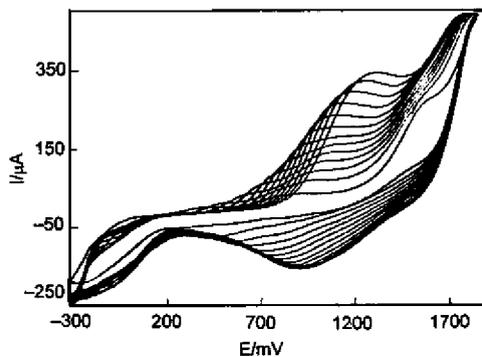


Figure 2. Cyclic voltammograms of 3-MET 1 mM-thiophene 1 mM mixture in  $\text{PhNO}_2$ ,  $0.1 \text{ Bu}_4\text{NPF}_6$ , GC disk electrode vs. Ag/AgCl, scan rate=50 mV/s (13 cycles).

were soluble in organic solvents. The solutions took a blue colouration and were stable in air. The chemical copolymerization condition was the same as the electrical copolymerization.

Figures 1–3 show the electrocopolymerization of 3-MET with aniline, thiophene and pyrrole by cyclic voltammetry of above conditions. Poly(3-MET) is relatively unstable on the GC disk electrode because either it is soluble in  $\text{PhNO}_2$  or it has not sufficient coplanarity. The oxidation-reduction potentials of copolymers are different from their homopolymers. Therefore, cyclic voltammograms confirm the

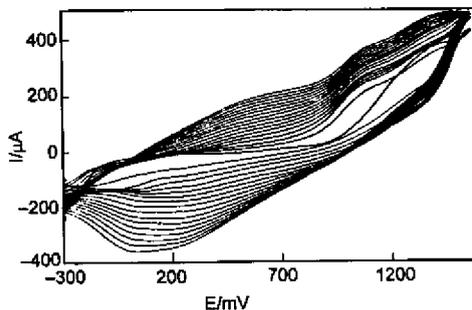


Figure 3. Cyclic voltammograms of 3-MET 1 mM-pyrrole 1 mM mixture in  $\text{PhNO}_2$ ,  $0.1 \text{ M Bu}_4\text{NPF}_6$ , GC disk electrode vs. Ag/AgCl, scan rate=50 mV/s (17 cycles).

formation of copolymers. Spectroscopy data certify the formation of copolymers in the chemical polymerization as well.

Figures 4<sub>a-c</sub> show that the anodic (ipa) and cathodic (ipc) peak current intensity via different scan rate (Ag/AgCl reference electrode) in -400-1000 mV potential ranges were linear. Therefore, the polymers are stable on the electrode surface and the redox reaction polymer films on electrode surface have surface absorption. The oxidation potentials of copolymers were reduced via poly(3-MET). The poly(3-MET) of copolymers have good electro-deposition behaviour on the GC electrode surface. Table 1 shows the oxidation-reduction potential of polymers obtained on electrode surface.

Scheme 1 shows the chemical or electrical copolymerization mechanisms. The same mechanism also rules for 3-MET with polyaniline.

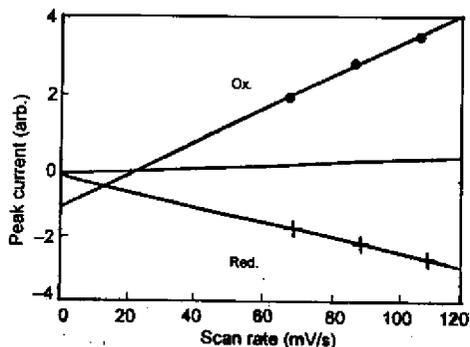
### Electronic Conductivity

The conductivity values obtained for poly(3-MET) and its copolymers, measured by four-point probe technique, are presented in Table 2. So that we have expected conductivity of copolymers higher than poly(3-MET). The polymer films possessed conductivities of  $<10^{-4}$ - $10^{-3}$  S/cm. After redoping with nitromethane solutions of 0.1 M  $\text{FeCl}_3$  or vapour  $\text{I}_2$  conductivities increased to  $10^{-3}$ - $10^{-2}$  S/cm. For both oxidants ( $\text{FeCl}_3$  or vapour  $\text{I}_2$ ) and for all four polymers the oxidized polymer films were relatively unstable and after one month of exposure to the ambient atmosphere the conductivity decreased and then it became constant.

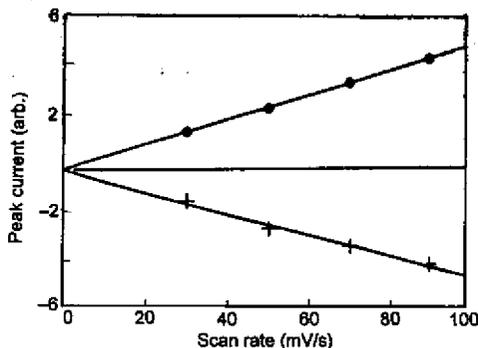
The electroactive copolymers as expressed by

**Table 1.** The oxidation-reduction potentials of polymers during electropolymerization.

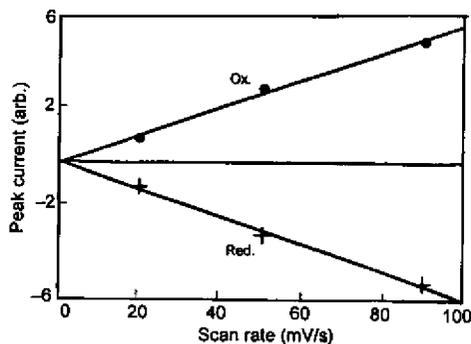
Samples	Monomer oxidation (mV)	Polymer oxidation (mV)	Polymer reduction (mV)
Poly(3-MET)	1600	600	-150
Poly(3-MET-co-Ani)	1188	400	-50
Poly(3-MET-co-Th)	1700	1200	900
Poly(3-MET-co-Py)	1150	550	200



(a)



(b)



(c)

**Figure 4.** The anodic and cathodic peak current vs. scan rate of a) poly(3-MET-co-Ani), b) Poly(3-MET-co-Py) and c) poly(3-MET-co-Th).

**Table 2.** The conductivity  $\delta$  of poly(3-MET) and its copolymers with aniline, thiophene and pyrrole measured by four-point probe method.

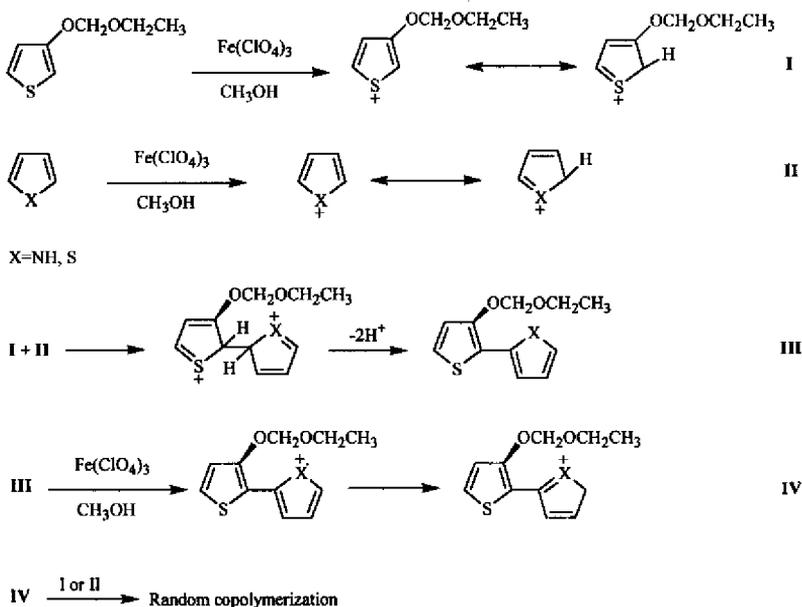
Polymer	Oxidant $\dagger$	Before doping $\delta$ (Scm $^{-1}$ )	After doping (vapour I $_2$ ) $\delta$ (Scm $^{-1}$ )
Poly(3-MET)	Fe(ClO $_4$ ) $_3$ .9H $_2$ O	$1.2 \times 10^{-4}$	$3.4 \times 10^{-3}$
Poly(3-MET-co-ANI)	*	$6.2 \times 10^{-4}$	$3.5 \times 10^{-3}$
Poly(3-MET-co-Th)	*	$8.0 \times 10^{-3}$	0.07
Poly(3-MET-co-Py)	*	$8.2 \times 10^{-3}$	0.04

the increase of the peak area and shift of other peaks to lower potentials via poly(3-MET). Poly(3-MET-co-Th) and poly(3-MET-co-Py) show more electroactivity even after 200 cycles whereas, the activity was reduced even before 30 cycles for poly(3-MET).

### UV-Visible Spectroscopy

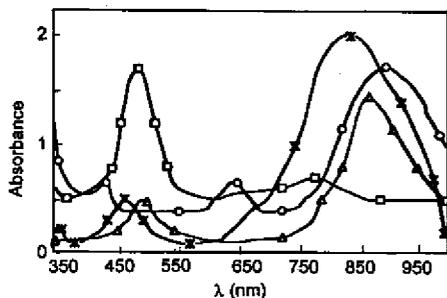
The visible absorption spectra of polymers were recorded and are shown in Figure 5. In the neutral state, polymers show a maximum of absorption at 450 to 650 nm that could be related to a quite highly

conjugated backbone. The colour of solution in this step became red. In the doped state, polymers exhibit a maximum of absorption at 650–900 nm that could be related to highly doping and solutions become blue. If the neutral state of polymers is increased the absorption peaks between 450 to 650 nm will increase and also absorptions between 650 to 900 nm will decrease. If the doped state of polymers is increased the absorption peaks between 650 to 900 nm will increase and also absorptions between 450 to 650 nm will decrease.

**Scheme I**

**Table 3.** The molecular weight distribution averages for the polymers.

Molecular weights	Poly(3-MET)	Poly(3-MET-co-Ani)	Poly(3-MET-co-Py)	Poly(3-MET-co-Th)
Number average	13259	26670	17760	33943
Weight average	35493	73456	53330	108617
Z-average	85962	214796	155944	317612
(Z+1)-average	146136	451071	249510	571707
Dispersity	2.6	2.7	3.0	3.2



**Figure 5.** Visible absorption spectra of the poly(3-MET)(□), poly(3-MET-co-Ani)(○), poly(3-MET-co-Th)(△) and Poly(3-MET-co-Py)(▲) in acetonitrile.

### Gel Permeation Chromatography (GPC)

The GPC of the poly(3-MET) and their copolymers were analyzed using polystyrene standard. The GPC curves obtained show a unimodal distribution. The molecular weight distribution averages for the polymers are presented in Table 3.

### CONCLUSION

This paper shows the way by which 3-methoxyethoxythiophene and its copolymers with aniline, thiophene and pyrrole it allows to obtain materials with a highly conjugated backbone. The produced copolymers via chemical and electrochemical methods are soluble in organic solvents such as dimethyl-

formamide dimethylsulphoxide and acetonitrile.

These copolymers very stable in the air for one month or a few more months. Further investigations are in progress to characterize these copolymers.

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