

Synthesis and Characterization of Novel Polythiophenes Containing Poly(ethylene oxide) Side Chains

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ABSTRACT: Thiophene copolymers and their derivatives with poly(ethylene oxide) side chains were synthesized. The starting monomers were 3-hexylthiophene and 2-(3-thienyl) ethanol with poly(ethylene oxide) grafted to the side chains. New functionalized polythiophenes were prepared by both chemical oxidation with FeCl_3 and electropolymerization.

The conjugating polymers were characterized. The structures of the polythiophene derivatives agreed with the design. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1803–1808, 2006

Key words: conducting polymers; synthesis

INTRODUCTION

In the class of conducting polymers, that is, polymers with π -conjugated backbones, polythiophenes are very interesting because of their good thermal and chemical stability and relative ease of functionalization, which potentially permit the fine tuning of their physical and electronic properties. Moreover, polyconjugated chains exhibit electrochromic and electronic behavior.^{1,2} In optoelectronic devices such as light-emitting diodes and batteries with these characteristics, the functionalization of polythiophenes with poly(ethylene oxide) (PEO) side chains may be of interest in an attempt to combine different interesting properties in one material and to achieve multifunctional polymers.

On the other hand, over the last few years, organic materials exhibiting electrochromic properties have been the subject of intense investigation for their possible technological applications.^{5–13} In particular, polymers containing PEO side chains attached chemically to the backbone seem to be very promising for these purposes. Some review articles have appeared recently on the applications of conducting polymers and conducting polyelectrolytes in the field of chemical sensors and biosensors.^{14–17}

Therefore, we focus in this article on ethylene oxide group substituted polythiophenes because of their processibility, grafting a PEO unit possessing a solva-

tion group to the end of a 3-alkyl chain of the thiophene ring to obtain a monomer with PEO. With chemical and electrochemical methods, the monomer was polymerized.

EXPERIMENTAL

Materials

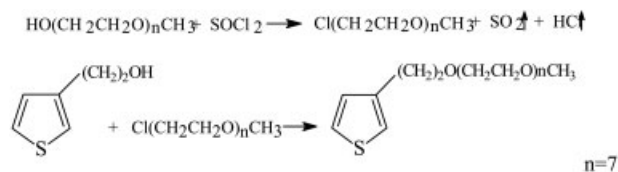
Poly(ethylene glycol) methyl ether (average molecular weight \approx 350) was purchased from Aldrich Chemical Co. and used as received. 2-(3-Thienyl) ethanol, 3-hexylthiophene, thiophene, iron(III) chloride, lithium perchlorate, nitromethane, and sodium hydride were also commercial products from Aldrich Chemical. They were used as received without further purification. Pyridine, thionyl chloride, absolute diethyl ether, hydrochloric acid, sodium sulfate (anhydrous), *N,N*-dimethylformamide (DMF), nitric acid, *n*-hexane, tetrahydrofuran, chloroform, carbon tetrachloride, toluene, ethanol, and acetone, from chemical reagent companies in China (analytical-reagent-grade), were used as received. Ammonium thiocyanate (analytical-reagent-grade) was acquired from Beijing Suanghuan Chemicals Factory (Beijing, China). Acetonitrile (ACN; analytical-reagent-grade; Beijing Yili Fine Chemicals Co., Ltd., Beijing, China) was dried and distilled over calcium hydride under argon. Tetrabutylammonium perchlorate (TBAP) was purchased from Fluka and was used without further purification.

Equipment

The electrochemical studies were carried out with an EG&G PAR model 237A potentiostat/galvanostat and a CH Instruments model 600 voltammetric analyzer.

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Scheme 1

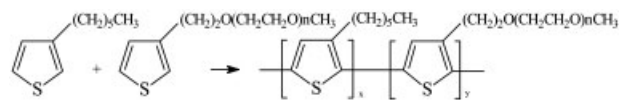
The electrochemical measurements were performed with a Pt wire as the working electrode. Ag/Ag⁺ or Ag wire as the reference electrode and platinum foil as the counter electrode were used in 0.1M TBAP or LiClO₄/ACN. Fourier transform infrared (FTIR) spectra of the monomers (pure liquids) and polymers on KBr plates or pressed KBr disks were taken with a 520 FTIR spectrometer from Nicolet. ¹H-NMR spectra [solution in dimethyl sulfoxide (DMSO)] were taken on a model AV 300 (300-Hz) NMR spectrometer from Bruker. Elemental analysis of C, H, O, Cl, and S was carried out with an Elementar GmbH (Germany) Vari-oEL analysis system.

Synthesis of the monomers

Poly(ethylene glycol) methyl ether chlorine was synthesized as reported earlier.^{16,17} For the synthesis of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether, 5 g (0.039 mol) of poly(ethylene glycol) methyl ether chlorine was stirred at 70°C under argon for 3 h in the presence of 1.05 equiv of 2-(3-thienyl) ethanol (15.1085 g) and 1.3 equiv of sodium hydride (1.2168 g) and DMF or ACN (25 mL). The mixture was cooled to room temperature, poured into an excess of water, and extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous sodium sulfate before the removal of ether and DMF at a reduced pressure to obtain the product as a liquid (see Scheme 1).

Chemical synthesis of the polymers or copolymers

A mixture of monomer 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether with 3-hexylthiophene or thiophene, in the adopted molar ratio, was oxidatively polymerized chemically with FeCl₃ in a mixture of nitromethane and carbon tetrachloride according to the following method. The monomer (10 mmol) was added dropwise over 20 min at room temperature to a suspension of 40 mmol (6.48 g) of anhydrous FeCl₃ in 80 mL of dry nitromethane and carbon tetrachloride. The mixture was stirred for over 4 h under a flow of dry nitrogen to eliminate the hydrochloric acid that evolved and was then treated with 300 mL of chloroform. The resulting organic phase was washed with 1M HCl up to the complete elimination of iron(III) ion (tested with ammonium thiocyanate). After the evap-



Scheme 2

oration of the solvent, the crude polymer was fractionated by precipitation with carbon tetrachloride from a toluene solution. The colors of the products ranged from red to blue-green with thiophene or 3-hexylthiophene added. The general structure of the corresponding copolymers is reported in Scheme 2.

RESULTS AND DISCUSSION

Chemical synthesis of the thiophene polymers

The copolymerization of thiophene or 3-hexylthiophene and 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether gave rise to materials insoluble in common organic solvents, whereas the use of the monomer 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether, which exerted a plastifying effect, made it possible to obtain soluble fractions. A marked increase in these fractions was observed in the homopolymerization when the CH₃NO₂/CCl₄ mixture was employed as the reaction medium instead of CHCl₃, which is generally used for substituted thiophenes.

FTIR spectroscopy studies

The synthesis process of poly(ethylene glycol) methyl ether chlorine was monitored by FTIR (Fig. 1). For the intermediate product, the characteristic absorption of hydroxyl group at 3338 cm⁻¹ was appreciably lowered, whereas two stronger characteristic absorptions

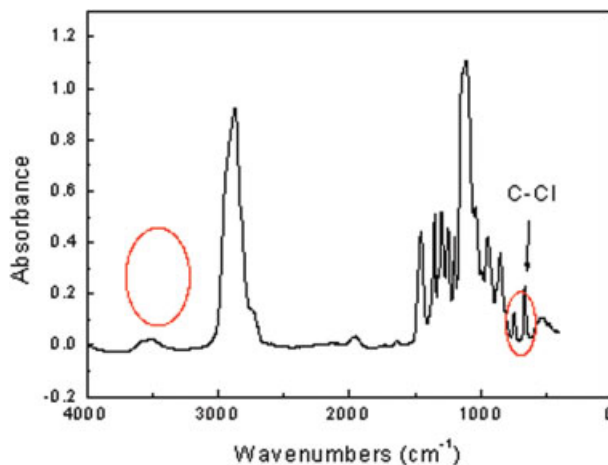


Figure 1 FTIR spectrum of poly(ethylene glycol) methyl ether chlorine after the first step of the reaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Assignment of the Main Absorptions in the IR Spectra of Poly(ethylene glycol) Methyl Ether and Poly(ethylene glycol) Methyl Ether Chlorine

Poly(ethylene glycol) methyl ether		
Absorption peak (cm ⁻¹)	Intensity	Assignment
3338	Very strong, wide	OH
2872	Strong, sharp	CH ₃
1453	Middle, sharp	CH ₂ and CH ₃
1249	Weak, sharp	C—O
1170	Strong, wide	C—O
1108	Strong, wide	C—O—O
1041	Middle, sharp	C—O
Poly(ethylene glycol) methyl ether chlorine		
Absorption peak (cm ⁻¹)	Intensity	Assignment
2872	Strong, sharp	CH ₃
1453	Middle, sharp	CH ₂ and CH ₃
1249	Weak, sharp	C—O
1170	Strong, wide	C—O
1108	Strong, wide	C—O—O
1041	Middle, sharp	C—O
744, 664	Weak, sharp	C—Cl

of the C—Cl bond at 744 and 664 cm⁻¹ were found. This was evidence that an appreciable number of the hydroxyl groups reacted. The absorption peak at 3338 cm⁻¹ was absent, and this indicated that the hydroxyl group was converted. In addition, there were strong absorptions at 744 and 664 cm⁻¹, showing that the product was a poly(ethylene glycol) methyl ether chlorine. The assignment of the main absorption bands appearing in the IR spectrum is given in Table I. A discernible absorption peak at 3338 cm⁻¹ sometimes appeared in the IR spectrum because of the incomplete conversion of the hydroxyl group. If the reaction time increased and the thionyl chloride was in excess of a given amount, no such peak could be detected; this showed that the product contained no free OH groups. In addition, the absorption of PEO crystallization bands at 1463, 1364, 1283, 1244, 1149, 1062, and 965 cm⁻¹ was absent. The results showed that poly(ethylene glycol) methyl ether chlorine was not crystallized.

The IR spectrum of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether, as the reaction product of poly(ethylene glycol) methyl ether chlorine with 2-(3-thienyl) ethanol, is shown in Figure 2. Comparing the IR spectra of the raw material and the product, we found that the IR spectrum of the raw material, 2-(3-thienyl) ethanol, had a very strong absorption peak of the hydroxyl group at 3350 cm⁻¹. That of poly(ethylene glycol) methyl ether chlorine had strong absorption peaks of C—Cl at 744 and 664 cm⁻¹. The characteristic

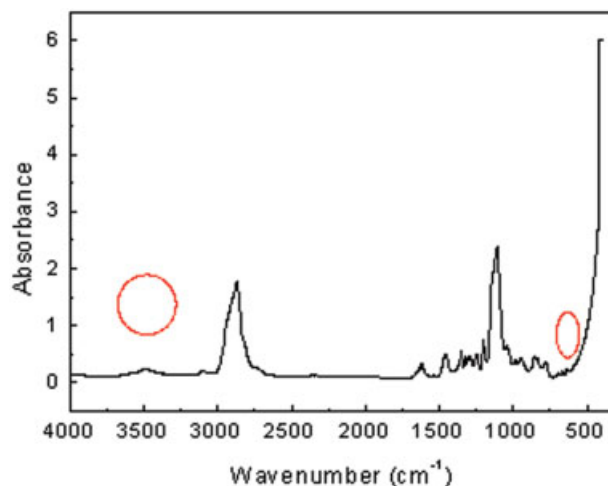


Figure 2 FTIR spectrum of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

absorptions of the hydroxyl group at 3338 cm⁻¹ and the C—Cl bond at 744 and 664 cm⁻¹ of the product, 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether, were absent. This was evidence that an appreciable number of the hydroxyl groups and C—Cl groups reacted and that 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether was synthesized. The assignment of the main absorption bands appearing in the IR spectrum is listed in Table II. In addition, the absorption of PEO crystallization bands at 1463, 1364, 1283, 1244, 1149, 1062, and 965 cm⁻¹ was absent. The results showed that 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether was also not crystallized.

The IR spectrum of the copolymer of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether with thio-

TABLE II
Elemental Analyses of Poly(ethylene glycol) Methyl Ether Chlorine (C₁₅H₃₁O₇Cl), 2-(3-Thienyl) Ethyl Poly(ethylene glycol) Methyl Ether (C₂₁H₃₈O₈S), and Poly[2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether] (C₂₁H₃₆O₈S)

		Calculated (%)	Found (%)	Relative error
				(%)
C ₁₅ H ₃₁ O ₇ Cl	C	50.20	51.02	1.63
	H	8.71	8.61	1.14
	O	31.21	30.64	1.82
	Cl	9.88	9.73	1.52
C ₂₁ H ₃₈ O ₈ S	C	55.97	55.91	0.11
	H	8.50	8.60	1.18
	O	28.41	28.53	0.42
	S	7.12	6.96	2.25
C ₂₁ H ₃₆ O ₈ S	C	56.23	56.11	0.21
	H	8.08	7.86	2.72
	O	28.54	29.01	1.65
	S	7.15	7.02	1.82

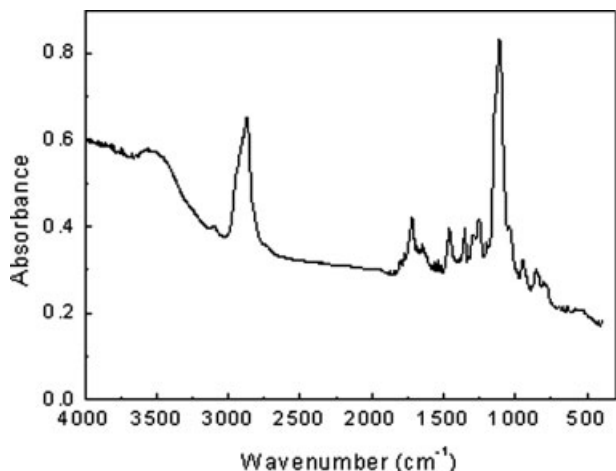


Figure 3 FTIR spectrum of the copolymer of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether with thiophene.

phene is shown as Figure 3. The characteristic absorptions of the copolymer of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether with thiophene are similar to those of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether.

Elemental analysis

Elemental analysis for the purified poly(ethylene glycol) methyl ether chlorine, 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether, and poly[2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether] was carried out (Table II). When these products were obtained, the formulas of the monomers and repeating unit in the polymer could be expressed as $C_{15}H_{31}O_7Cl$, $C_{21}H_{38}O_8S$, and $C_{21}H_{36}O_8S$ for poly(ethylene glycol) methyl ether chlorine, 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether, and poly[2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether], respectively, corresponding to the structures given in Schemes 1 and 2.

1H -NMR spectroscopy

Figure 4 shows the 1H -NMR spectrum of poly(ethylene glycol) methyl ether chlorine with the attributions of the signals with respect to the protons. In Figure 4, the peak at 2.5 ppm was assigned to the methylene protons of DMSO. The peak at 3.3 ppm was assigned to DMSO in water. The peak at 3.24 ppm was assigned to the methyl protons of poly(ethylene glycol) methyl ether chlorine. The multiplet at 3.5–3.57 and 3.44–3.41 ppm was assigned to the methylene protons of CH_2-CH_2O . The multiplet at 3.65–3.72 ppm was assigned to the methylene protons of $Cl-CH_2-$.

2-(3-Thienyl) ethyl poly(ethylene glycol) methyl ether was synthesized with poly(ethylene glycol) methyl ether chlorine and 2-(3-thienyl) ethanol. The

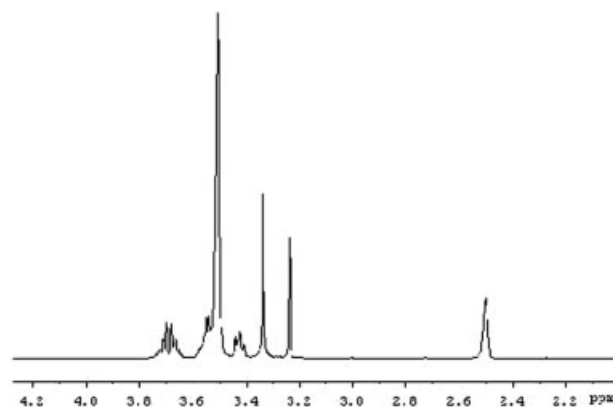


Figure 4 1H -NMR spectrum of poly(ethylene glycol) methyl ether chlorine in DMSO.

1H -NMR spectrum of 2-(3-thienyl) ethanol is shown as Figure 5. By a comparison of Figure 5 with references or calculated values, every peak in Figure 5 was assigned as follows: 2.5 ppm to the methyl protons of DMSO, 3.3 ppm to DMSO in water, 2.71–2.76 ppm to the methylene protons of $-CH_2-OH$, 3.57–3.64 ppm to the proton of the hydroxyl group, 4.63–4.67 ppm to the methylene protons of the attached thiophene ring, and 7.00–7.02, 7.17–7.18, and 7.41–7.43 ppm to the protons of the 4-, 5-, and 2-locations of the thiophene ring.

The 1H -NMR spectrum (300 MHz, DMSO) of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether is shown in Figure 6. The peaks were assigned by comparison with the spectra of 2-(3-thienyl) ethanol and poly(ethylene glycol) methyl ether chlorine as follows: 2.5 ppm to the protons of DMSO, 3.3 ppm to DMSO in water, 2.79–2.84 ppm to $-CH_2-$ of $-CH_2-OH$ after the reaction, 3.24 ppm to $-CH_3$ of the methoxyl group, 3.5–3.57 and 3.44–3.41 ppm to the protons of $-CH_2-CH_2O-$, 4.63–4.67 ppm to the methylene protons of the attached thiophene ring, and 7.00–7.02, 7.17–7.18, and 7.41–7.43 ppm to the protons of the 4-,

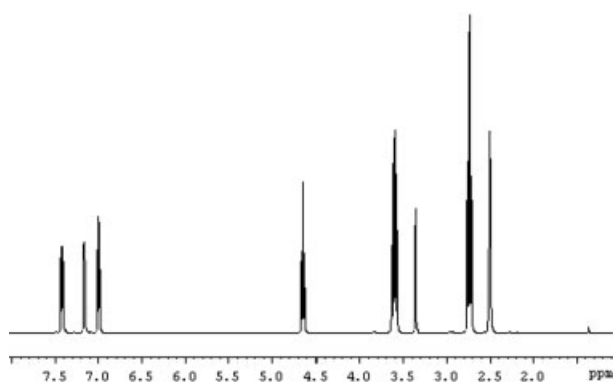


Figure 5 1H -NMR spectrum of 2-(3-thienyl) ethanol in DMSO.

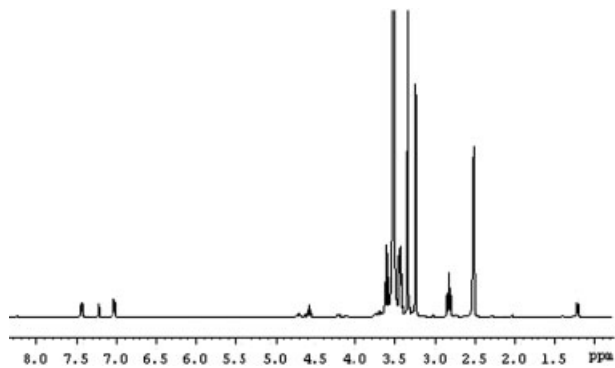


Figure 6 $^1\text{H-NMR}$ spectrum of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether in DMSO.

5-, and 2-locations of the thiophene ring. However, the peaks at 3.57–3.64 ppm ($-\text{OH}$) and at 3.65–3.72 ppm ($\text{Cl}-\text{CH}_2-$) were absent, and this was evidence that 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether was synthesized by the reaction of 2-(3-thienyl) ethanol and poly(ethylene glycol) methyl ether chloride.

Finally, poly[2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether] was synthesized with a chemical method. Its $^1\text{H-NMR}$ spectrum is shown in Figure 7. The peaks were assigned by comparison with the spectra of the monomers. However, the peaks at 7.17–7.18 and 7.41–7.43 ppm (the protons of the 5- and 2-locations of the thiophene ring) were absent. This was also evidence that poly[2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether] was polymerized by means of a chemical method.

Electropolymerization

2-(3-Thienyl) ethyl poly(ethylene glycol) methyl ether was synthesized from hydroxymethylene by the standard etherification reaction with sodium hydride in dry DMF or ACN, as shown in Scheme 1. The structure of the monomer was confirmed by NMR spectroscopy, elemental analysis, and FTIR. 2-(3-Thienyl) ethyl poly(ethylene glycol) methyl ether was then electropolymerized with a 10 mM solution of the

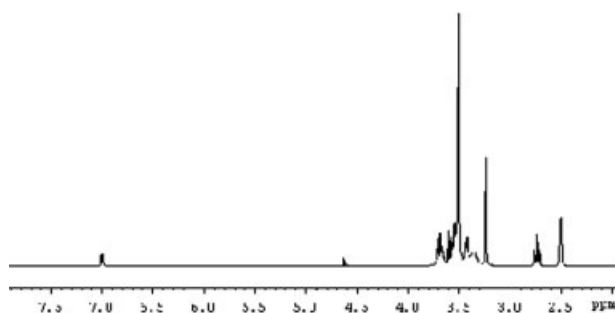


Figure 7 $^1\text{H-NMR}$ spectrum of poly[2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether] in DMSO.

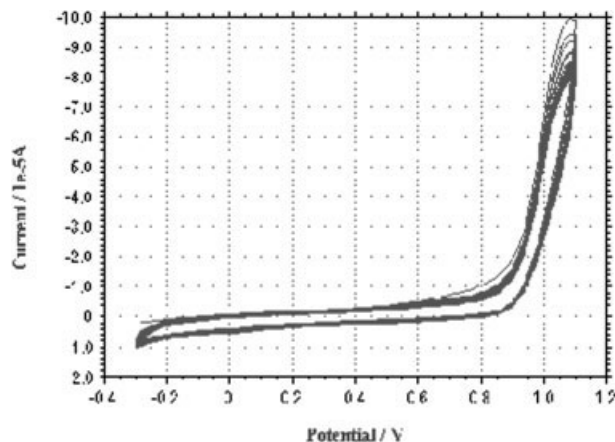


Figure 8 Repeated potential scan electropolymerization of 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether at 100 mV/s in 0.1M TBAP/ACN. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

monomer [thiophene/2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether = 4:1 mol/mol] in 0.1M TBAP/ACN by the cycling of the potential, at 100 mV/s, between -0.6 and 1.2 V versus Ag/Ag^+ on a platinum wire. The monomer oxidation peak at the bare electrode started at 0.9 V and peaked at 1.1 V (Fig. 8). Thiophene/2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether was oxidized with increasing cycling numbers, and the oxidation peak increased gradually. This indicated that the electroactive polymer was formed. After monomer oxidation in consecutive cycles, polymer redox waves [did not develop well. This indicated that an electroactive polymer film did not form on the electrode surface. Such an effect was observed previously for 3,4-ethylenedioxythiophene polymers substituted with bulky groups.⁵ The presence of a bulky group on the monomer resulted in the formation of polymers with an open morphology that facilitated the fast movement of the counterion in the polymeric structure.

Thiophene/2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether was synthesized with a 10 mM solution of the monomer in 0.1M TBAP/ACN by the constant-current method, at a current intensity of 0.01 or 0.03 mA/cm^2 , on platinum over 15 min (Fig. 9). A blue-black copolymer film was formed on the platinum electrode. This indicated that the electrochemical polymerization could process at room temperature. Changing a component of the electrolyte solution (e.g., different anions), we could form different doping polymers.

CONCLUSIONS

Conjugating polymers of thiophene derivatives was found to be a viable method for the preparation of

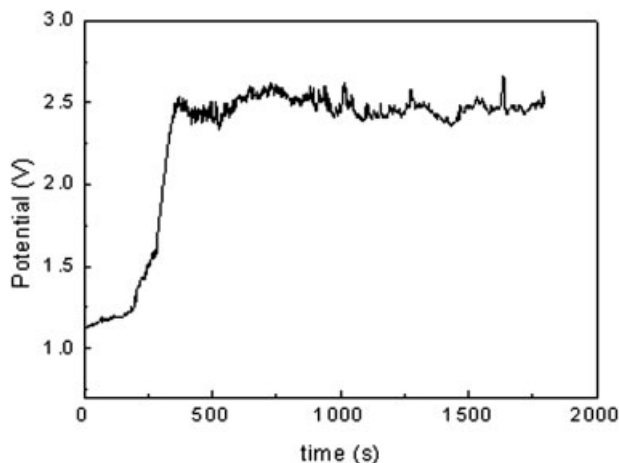


Figure 9 Time-voltage plot of the constant-current polymerization of thiophene and 2-(3-thienyl) ethyl poly(ethylene glycol) methyl ether at 0.03 mA in 0.1M TBAP/CAN.

new polythiophenes functionalized with PEO side chains. The composition and structure of the polymers and monomers were determined by NMR spectroscopy, IR spectroscopy, and elemental analysis. We found that PEO side-chain substitution on a thiophene ring would further improve the properties of polythiophenes and might result in better conjugating polymers. Work is in progress in this direction.

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