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ELECTROSYNTHESIS OF POLY (SELENOPHENE-CO-THIOPHENE) FILMS IN BORON TRIFLUORIDE DIETHYL ETHERATE/ETHYL ETHER

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Abstract. Electrosynthesis of selenophene-thiophene copolymers was successfully realized at constant electrode potential in a binary solvent system consisting of boron trifluoride-ethyl ether and an additional amount of ethyl ether (mole ratio 1:2). The homo- and copolymer films obtained were studied and characterized with cyclic voltammetry and FTIR spectroscopy. The influence of the applied polymerization potential and the monomer feed ratio of selenophene and thiophene on the copolymer materials was investigated. The obtained films demonstrate a good stability of the redox activity in acetonitrile-based electrolyte solution.

Keywords: electropolymerization, conducting copolymers, polythiophene, polyselenophene, cyclic voltammetry.

1. Introduction

Conducting polymers are an interdisciplinary research area. The field has developed during the last 30 years due to an interest in academic research as well as in possible commercial applications and possibility of combining new chemical functions in a backbone [1]. The diverse applications of conducting polymers in materials for battery electrodes [2], gas sensors [3], chemical sensors [4-11], biosensors [12-15], ion sieving [16], corrosion protection [17], and microwave shielding [18] has led to numerous researches on conjugated polyacetylenes, polythiophenes, polypyrroles, polyanilines, polyphenylenes, and some others. This opened new fields of application for macromolecules with the aim of improving both the electrical conductivity and the stability of the materials.

Polythiophenes are the most studied conducting polymers [19]. They have acquired remarkable technological potentials in electrocatalysis [20, 21], fabrication of molecular electronic devices [22], solid state batteries [23], chemically modified electrodes [24], and biosensors [25-27].

In spite of the huge number of papers published on polythiophenes, very little is known about their close analogue polyselenophene and its derivatives. Computational studies exposed that polyselenophenes should have lower band gap, more quinoid character, and more rigid backbone than polythiophenes. The possible advantages of polyselenophenes are attributed to the distinctive properties of the Se atom comparing with S atom. Selenophene has intermolecular Se---Se interactions, selenophene monomers have lower oxidation and reduction potentials than thiophenes, Se atom is larger size and more easily polarized than sulfur, polyselenophenes should be able to accommodate more charge upon doping than polythiophenes [28- 31].

Polyselenophene has been synthesized previously and its chemical, electrochemical, and optical properties were investigated [32-39]. However, no reasonably conducting polyselenophene was reported in the last decade.

The electrosynthesis of heterocyclic monomers in common organic media, such as acetonitrile, nitromethane or propylene carbonate, leads to the poor quality of conducting films [28]. Two possible approaches were reported to reduce the monomers oxidation potentials. One is the substitution on β -position of aromatic ring [40, 41] with relatively low band gap, mainly by substitution of electron donating groups. The other is replacement of common organic media with middle strong Lewis acid, such as boron trifluoride diethyl etherate (BFEE) [42-44].

Free-standing polyselenophene films have been successfully synthesized by electrochemical polymerization of selenophene at low potential ($E_{SCE} = 1.23$ V) from distilled boron trifluoride diethyl etherate (BFEE). The polymer shows good mechanical properties; its electrical conductivity is around 0.28 S cm^{-1} [28].

Weaknesses in mechanical, physical and chemical properties of polymers can be eliminated through copolymerization process. Copolymerization is basically

integration of two or more different structures in a polymer chain. The usefulness of copolymerization technique is due to the different properties of the resulting materials than those of the corresponding homopolymers [45]. Concentration of monomer in the feed determines physical and chemical properties of copolymer. Hence, controlling concentrations of monomers can lead to copolymers with desired properties [46].

Copolymers of furan and thiophenes were successfully electro-copolymerized. The obtained copolymers were characterized by cyclic voltammetry, Infrared spectroscopy, Raman spectroscopy, UV-Visible spectroscopy, and electrical conductivity measurements [47-51]. The copolymers showed improved properties in comparison with polyfuran. Aniline-thiophene copolymers have attracted attention because of the apparently high stability of the oxidized form of the copolymer identified from the highly reversible switching of the conductivity [52].

The derivatives like poly(biselenophene) [53], poly[1,2-bis(2-seleninyl)ethane] [54], oligoselenophenes [55], and the copolymers [56] with pyridine [57] were also tested for polymerization and the characterizations of corresponding polymers with special properties, such as nonlinear optical [58].

In connection with our work on selenophene-thiophene copolymers [59], results of electrosynthesis and electrochemical behavior of homo- and copolymer films of selenophene and thiophene in a binary solvent system consisting of boron trifluoride-ethyl ether and an additional amount of ethyl ether (mole ratio 1:2) are reported. The influence of the applied polymerization potential and the monomer feed ratio on the properties of the copolymers is discussed. The effect of using binary solvent system instead of common organic solvent, such as acetonitrile, is also investigated. In addition, a mechanism of the electrochemical formation of selenophene-thiophene copolymers is proposed based on already known coupling reactions of aromatic compounds. The stability of the redox activity of the obtained copolymers is investigated and compared with homopolymer films. Taking this into consideration, these new materials may appear more suitable for technological applications.

2. Experimental

Selenophene (TCI, 98 %) and thiophene (Acros, 99 %) were distilled under nitrogen just prior to use. Ethyl ether (EE) (Fisher Scientific) was dried and distilled in the presence of sodium. Boron trifluoride-ethyl ether (BFEE) (Acros, 48 % BF_3) was used as received. Tetrabutylammonium tetrafluoroborate (TBATFB) (Acros, 98 %) was dried under vacuum at 353 K for 24 h. Acetonitrile (Merck, anhydrous, < 10 ppm H_2O) was used without further purification.

The electrochemical polymerizations and examinations were performed in a one-compartment three-electrode cell by the use of a model 150 potentiostat-galvanostat (bio-logic) under computer control (EC-Lab) software. A platinum disc electrode was used as working electrode; and saturated calomel electrode (SCE) as reference electrode.

The obtained films were grown potentiostatically in BFEE + EE (ratio 1:2) solution containing in addition 0.1 M TBATFB as supporting electrolyte at room temperature at constant electrode potential for 2 min. The constant electrode potential for the preparation of copolymer films was chosen according to the threshold polymerization potential of the homopolymers. After polymerization the film was washed with acetonitrile to remove any traces of mono- and oligomers. Cyclic voltammetry of the polymers was carried out in a monomer free acetonitrile solution containing 0.1 M TBATFB as supporting electrolyte.

Before each polymerization, the platinum disc electrode was carefully polished with diamond polishing paste down to 0.1 μm and then to 0.05 μm with aqueous alumina slurry and cleaned with water and acetone, successively, and then dried by a blower. All solutions were deaerated by a dry N_2 stream for 10 min before the experiment and a slight N_2 over-pressure was maintained during the experiment.

For FTIR spectroscopy data, the pristine film was scraped off from the electrode and dried. FTIR spectra of the homo- and copolymer films using KBr-discs were recorded on Shimadzu FT-IR 8400 spectrometer at 2 cm^{-1} resolution.

3. Results and Discussion

3.1. Electropolymerization of Homo- and Copolymer Films

The two freshly distilled selenophene and thiophene was tested to be very stable during the whole experiment and can be directly used for the electrochemical polymerization of homo- and copolymer films.

Fig. 1 shows the anodic polarization curves of monomers in BFEE + EE (ratio 1:2) solution containing in addition 0.1 M TBATFB. The background electrolyte is electrochemically silent in the whole potential range. The lowest potential needed to sustain growth of a polymer layer of selenophene (threshold polymerization potential) is initiated at $E_{\text{SCE}} = 1.35 \text{ V}$ (curve B), lower than that of thiophene $E_{\text{SCE}} = 1.55 \text{ V}$ (curve A).

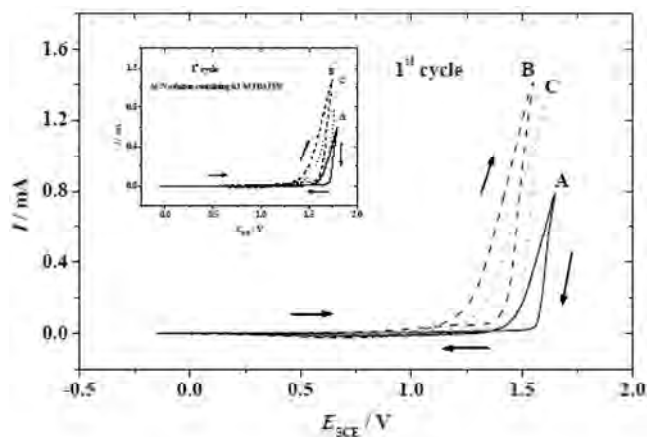


Fig. 1. CVs of 0.1 M thiophene (A); 0.1 M selenophene (B); 0.1 M selenophene and 0.1 M thiophene in 0.1 M TBATFB in BFEE + EE (ratio 1:2) (C); $dE/dt = 100$ mV/s

The lower the monomer oxidation onset, the less possible the kink coupling, such as α - β coupling and overoxidation. Thus, the quality of as-formed conducting polymers would be improved. This result implied that the replacement of sulfur by selenium would have a positive effect on the final conducting polymers [28].

The small difference between the oxidation potentials of the two monomers suggests a large probability of copolymerization of the two monomers. Curve C was obtained when a current-potential curve was taken in a solution containing 0.10 M selenophene and 0.10 M thiophene. However, the superposition of curve A and curve B does not simply add up to curve C. This might be caused by changes in the electrochemical environment such as electrode roughness [60, 61]. The oxidation potential of the mixture of selenophene and thiophene is around $E_{SCE} = 1.40$ - 1.45 V, which is between the oxidation potentials of the two monomers, implying that oxidation of both monomers is likely, the copolymer chains may accordingly be composed of selenophene and thiophene units [47, 50, 60].

Boron trifluoride-ethyl ether (BFEE) complex was used as a binary system to lower the oxidation potential of various aromatic monomers [43]. The significant decrease in the oxidation potential of selenophene and thiophene in the strongly acidic medium can be explained in two ways: first, the sulfur and selenium atom of the two monomers has a pair of free electrons that can be coordinated with BF₃. The strong electrophilic property of BF₃ lowered the oxidation potential of selenophene from $E_{SCE} = 1.55$ V in ACN solution to $E_{SCE} = 1.35$ V when using the binary system, whereas the oxidation onset of thiophene decreased by 0.15 V upon using BFEE/EE medium. Second, the increased acidity of the solvent imparts a greater stability to the cation radical, which in turn promotes the electrooxidation and subsequent polymerization process. It is clearly observed that the anodic

current increased by 30% when using the binary solvent system instead of common organic solvent such as CAN, which means the amount of the polymer deposited on the electrode is also increased (see the inset in Fig. 1). Ethyl ether was added to adjust the acidity of BFEE and the undesirable polymerization (precipitation of nonconjugated polymer chains) was suppressed [47, 54].

3.2. Electrochemistry of Homo- and Copolymer Films

The electrochemical behaviors of the homopolymer films deposited electrochemically were studied in acetonitrile-based electrolyte solution (Fig. 2).

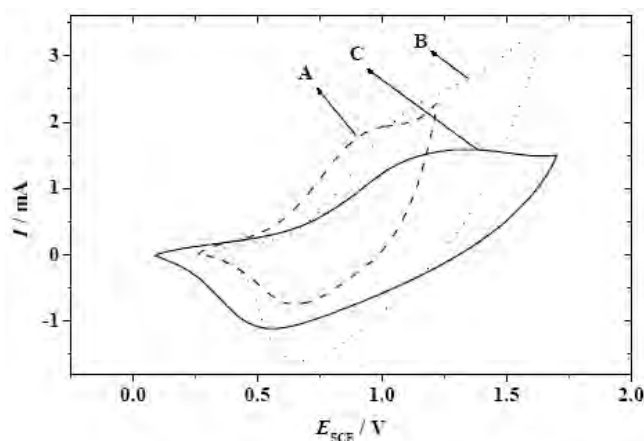


Fig. 2. CVs recorded in a monomer free acetonitrile solution + 0.10 M TBATFB polyselenophene deposited at $E_{SCE} = 1.35$ V in a BFEE + EE (ratio 1:2) containing 0.1 M selenophene; copolymer deposited at $E_{SCE} = 1.50$ V in a BFEE + EE (ratio 1:2) solution containing 0.1 M selenophene and 0.1 M thiophene (B) and polythiophene deposited at $E_{SCE} = 1.55$ V in a BFEE + EE (ratio 1:2) containing 0.1 M thiophene (C); $dE/dt = 100$ mV/s

Similar to the results in the literature [28, 47, 50], the steady-state CVs represent broad anodic and cathodic peaks. For polyselenophene (A), there is a broad anodic peak at $E_{SCE} = 0.94$ V caused by polymer oxidation and a corresponding broad cathodic peak around $E_{SCE} = 0.67$ V due to polymer reduction. Polythiophene (C) can be oxidized and reduced from 1.28 and 0.56 V. The broad redox waves in their CVs are commonly observed in the electrochemistry of intrinsically conducting polymers and can be interpreted due to the diffusion of the dopant ions in and out of the film as well as to the presence of coupling defects distributed statically, which results in a series of energetically nonequivalent chain segments [47, 50, 62-63].

Copolymerization is carried out potentiostatically. Fig. 2B shows a typical cyclic voltammogram of a copolymer obtained from solution containing 0.10 M

selenophene and 0.10 M thiophene prepared at $E_{SCE} = 1.50$ V.

Only one anodic/cathodic peak couple appears with the copolymer film at a position quite different from the positions observed with homopolymers. The appearance of one redox peak implies that only a single redox process occurs, the copolymer thus behaves uniformly (instead of two redox processes as observed with *e.g.* a heterogeneous mixture or a composite material) [50]. In addition it is noteworthy that both the cathodic and the anodic current are higher than those found with the homopolymers. Taking the peak current as an indicator of redox capacity this implies that the amount of deposited copolymer is higher after the same time of electropolymerization (2 min). The copolymer is more stable and less affected by overoxidation presumably due to the existence of thiophene units in the copolymer chains which may increase the stability of the film.

The CV also show a pronounced hysteresis, *i.e.*, a considerable difference between the anodic and cathodic peak potentials, up to 0.46 V, as shown in Fig. 2B. The main reasons accounting for this phenomenon are usually as follows: slow heterogeneous electron transfer, effects of local rearrangements of polymer chains, and slow mutual transformations of various electronic species [28, 63].

Electrochemical copolymerization both at different potentials and with different thiophene concentrations was investigated. Fig. 3 shows CVs of the copolymers obtained with electropolymerization in solutions containing 0.1 M selenophene and 0.1 M thiophene at potentials ranging from $E_{SCE} = 1.4$ to 1.6 V. The anodic peak potential of the copolymers shifts to higher values with increasing polymerization potential of the copolymer films. When prepared at $E_{SCE} = 1.4$ V, the copolymer shows an anodic peak at $E_{SCE} = 1.04$ V and cathodic peak at $E_{SCE} = 0.75$ V, whereas the copolymer prepared at $E_{SCE} = 1.6$ V shows redox peaks at $E_{SCE} = 1.21$ V and at $E_{SCE} = 0.63$ V, respectively. The former peak pair is closer to polyselenophene, whereas the latter film material is closer to polythiophene. This indicates that more thiophene units are incorporated into the copolymer chain with increasing preparation potential.

The electrochemical characteristics of both the homopolymers and copolymers displayed in Figs. 2 and 3 indicate that keeping the potential of electrosynthesis of copolymers formed in mixed solutions near the threshold potential for electropolymerization of selenophene may result in the selenophene-based copolymers and vice versa.

When the selenophene/thiophene feed ratio is changed from 1:1 to 3:1 (0.1 M/0.033 M) CVs as shown in Fig. 4A are obtained; at a ratio of 6:1 (0.1 M/0.0166 M) CVs shown in Fig. 4B result. Only one redox peak couple appears attributed to the *p*-doping/*n*-doping processes of the films. Up shift of the anodic peak with increasing preparation potentials is also observed. When comparing

CVs of the copolymers prepared at the same polymerization potential with different monomer feed ratio, the lower concentration of thiophene leads to a negative shift of the anodic peak potentials of the copolymer. This implies that more thiophene units are incorporated into the copolymer film when the concentration of thiophene increases (see Fig. 5).

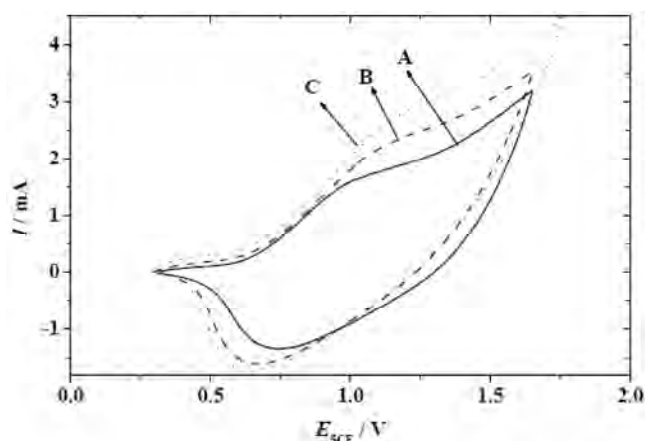


Fig. 3. CVs recorded in a monomer free acetonitrile solution + 0.10 M TBATFB of copolymers deposited at $E_{SCE} = 1.40$ V (A); 1.50 V (B) and 1.60 V (C) in a BFEE + EE (ratio 1:2) solution containing selenophene: thiophene (mole ratio 1:1); $dE/dt = 100$ mV/s

The peak potential values of the copolymers prepared at different potentials from these three different solutions are listed in Table 1, the peak potentials of homopolymers are added for comparison. All the above results indicate that the electrochemical properties of the copolymers depend not only on the electrochemical polymerization potential but also on the monomer feed ratio. Apparently the dependence of the electrochemical properties of the copolymer on the electropolymerization potential and monomer feed ratio reflects the composition and perhaps even the structure of the copolymers [47-51, 59].

Fig. 6 shows CVs at $dE/dt = 25, 50, 75$ and 100 mV/s of copolymer films deposited at $E_{SCE} = 1.50$ V in a solution containing 1:1 monomer ratio. The redox currents are proportional to the scan rates (inset), indicating a redox coupling fixing on the electrode and the electrochemical processes are diffusion-controlled [44, 64]. For a diffusion-controlled process the straight line should pass through the origin, but in the case of conducting polymers deviations from the ideal behavior may arise from contributions such as double-layer charging, which can disturb the zero intercept [65].

The electrochemistry of the deposited polymer films is further supported with observations and suggestions by results obtained with conductivity measurements (more detailed discussion will be published soon).

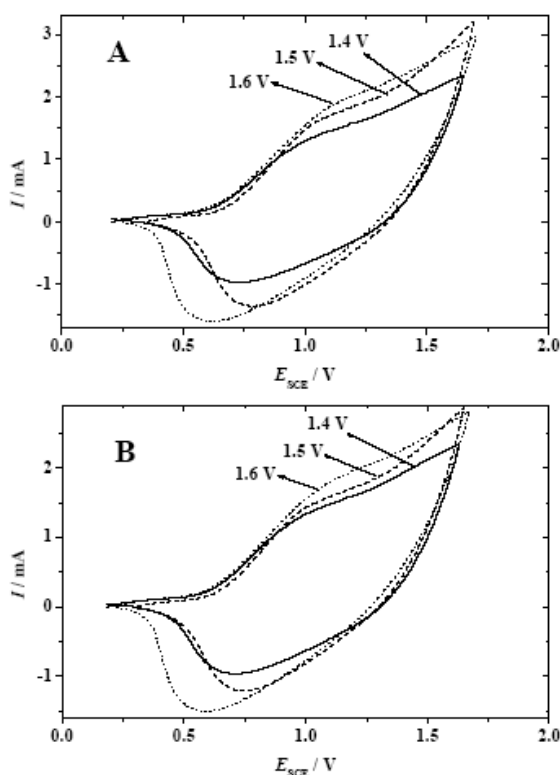


Fig. 4. CVs recorded in a monomer free acetonitrile solution + 0.10 M TBATFB of copolymers deposited at ranging $E_{SCE} = 1.6$ – 1.7 V respectively in a solution containing selenophene: thiophene mole ratio 3:1 (A) and 6:1 (B); $dE/dt = 100$ mV/s

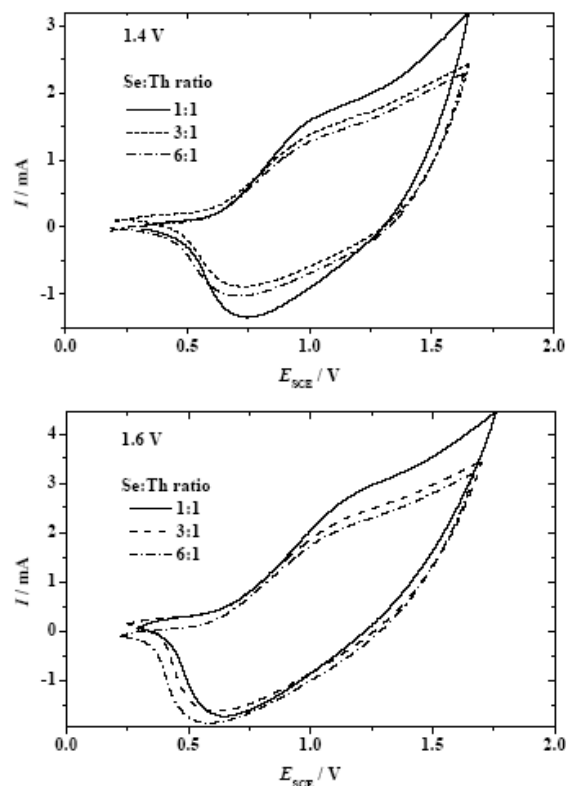


Fig. 5. CVs recorded in a monomer free acetonitrile solution + 0.10 M TBATFB of copolymers deposited at $E_{SCE} = 1.40$, 1.60 V respectively in a BFEE + EE (ratio 1:2) solution containing selenophene: thiophene (mole ratio 1:1, 3:1, 6:1); $dE/dt = 100$ mV/s

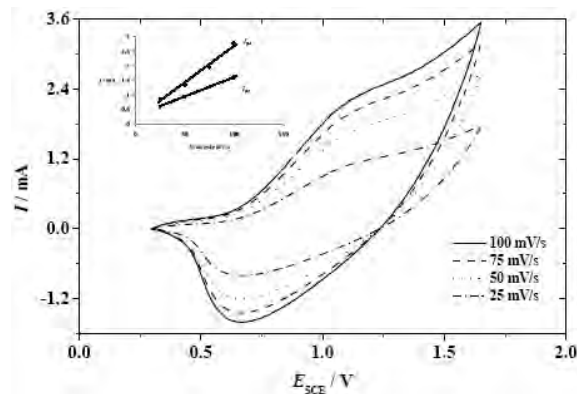
Table 1

Peak potentials of the copolymers prepared at various electropolymerization potentials E_{pol} from acetonitrile solutions containing different monomer feed ratio*

Se/Th (Mole ratio)	$E_{pol} = 1.40$ V		$E_{pol} = 1.50$ V		$E_{pol} = 1.60$ V		Polyselenophene $E_{pol} = 1.35$ V		Polythiophene $E_{pol} = 1.55$ V	
	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V
1:1	1.04	0.75	1.14	0.68	1.21	0.63	0.94	0.67	1.28	0.56
3:1	1.10	0.72	1.08	0.76	1.13	0.62				
6:1	0.97	0.71	1.03	0.74	1.10	0.59				

* Peak potentials of homopolymers are added for comparison.

Fig. 6. CVs recorded in a monomer free acetonitrile solution + 0.10 M TBATFB of copolymer films deposited at $E_{SCE} = 1.50$ V in a BFEE + EE (ratio 1:2) solution containing 0.1 M selenophene and 0.1 M thiophene; $dE/dt = 25$, 50 , 75 , and 100 mV/s



3.3. Stability of Redox Activity of Homo- and Copolymer Films

Selenophene-thiophene copolymers confirm practically a good long-term stability of redox activity after cycling in acetonitrile comparing with polyselenophene film. As shown in Fig. 7 the peak separation of anodic and cathodic peak potential is almost small which indicates a reversible redox process. The obtained films can be cycled repeatedly between the oxidized and neutral state with no significant decomposition of the materials.

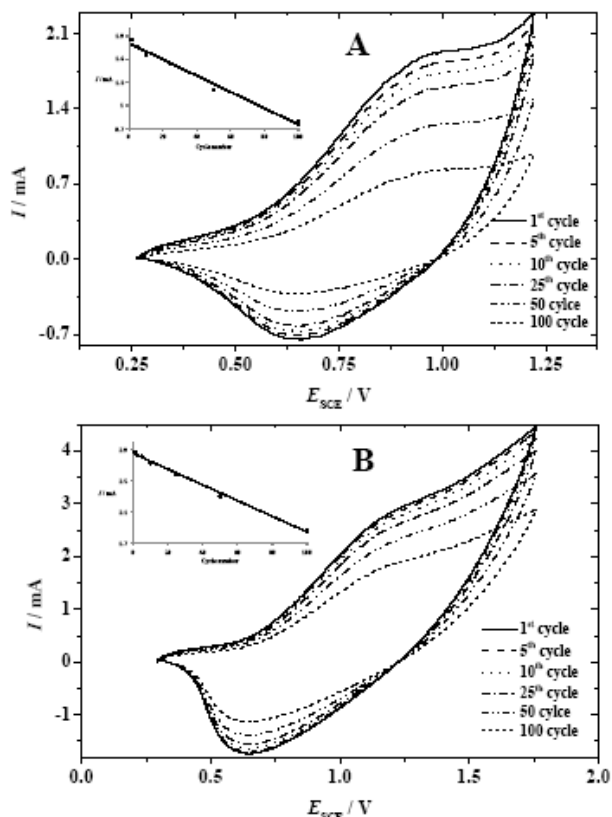


Fig. 7. 1st, 5th, 25th, 50th, and 100th CVs recorded in a monomer free acetonitrile solution + 0.10 M TBATFB of polyselenophene (A) and copolymer (B) deposited at $E_{SCE} = 1.60$ V in a BFEE + EE (ratio 1:2) solution containing Se: Th, mole ratio 1:1; $dE/dt = 100$ mV/s

The retention of the redox activity of copolymer film after cycling in dry acetonitrile for 100 times is about 65 % as compared to 43 % for selenophene homopolymer indicating the coexistence of both long and short conjugation lengths in the polymer chains. As shown in the insets the anodic peak current decreases as the number of potential cycles increases indicating a decrease of the redox activity. Additionally, the stability of the copolymer film declined gradually after exceeding 50 cycles while polyselenophene stability decreased obviously further than 25 cycles (Fig. 8).

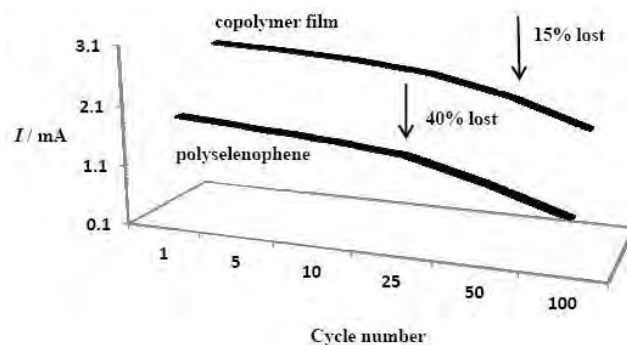
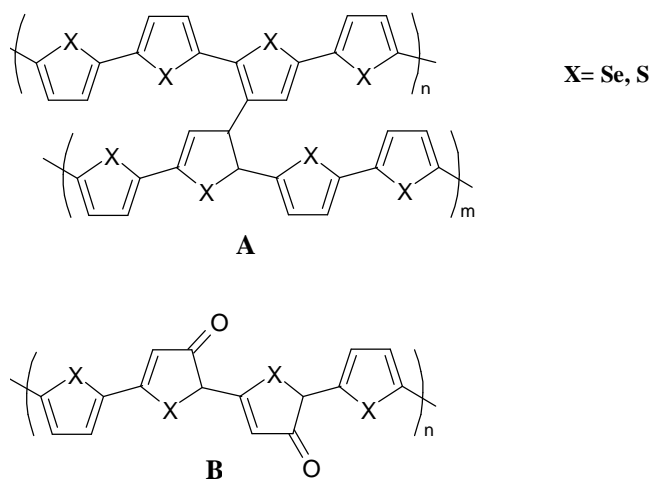


Fig. 8. Dependence of redox activity of polyselenophene and copolymer deposited at $E_{SCE} = 1.60$ V in a BFEE + EE (ratio 1:2) solution containing Se: Th, mole ratio 1:1 on cycle numbers

It is well known that the degradation of conducting polymers is a complex process and the mechanism of degradation is not clear yet. With polypyrrole and polythiophene degradation proceeds mostly at electrode potentials positive to the range wherein deposition and reversible redox cycling take place, thus reversible redox processes and the irreversible degradation process can be distinguished clearly [66]. When polyselenophene and copolymer film are cycled in dried acetonitrile solution the degradation process takes place in the same potential range in which the reversible redox process occurs. This implies that the degradation of conjugated structures occurs when the obtained films are oxidized from its undoped state to a doped state. The loss of the electrochemical activity of co-polymer in acetonitrile solutions might be related to the production of saturated C-H structures in the co-polymer chains (Scheme 1 (A)) [49, 67].



Scheme 1. Possible defects in the copolymer cycled in: dry acetonitrile solution (A) and aqueous solution (B)

To study the effect of the polymerization medium on the redox stability of homo- and copolymer films, Fig. 9 is included. The replacement of common organic media with middle strong Lewis acid, such as BFEE, resulted in lowering the oxidation onsets of these monomers. They are much lowered than those in acetonitrile containing small inorganic anions, such as BF_4^- , ClO_4^- and BF_6^- . Consequently, using binary solvent system (BFEE/EE) would enhance and improve the redox capacity of the obtained films. Furthermore, copolymerization between selenophene and thiophene developed and increased the electrochemical stability of polyselenophene due to the coexistence of thiophene units in the copolymer chains which may raise the conjugation lengths of the resulted materials.

However, when the copolymer film is cycled in an aqueous solution, the redox activity is totally lost and a very large anodic peak current around 1.45 V appears, without associated cathodic one (Fig. 10). This process is independent of pH value of the aqueous solution indicating that water molecules instead of protons or hydroxyl ions are involved in this degradation process

[47, 67]. Moreover, the redox activity of the copolymer film is strongly affected when the CV recorded in wet acetonitrile (H_2O : 1 % by volume). The associated loss of redox capacity during the oxidation process may be caused by the destruction of conjugated structures.

In wet acetonitrile and aqueous solution, the degradation by the nucleophilic mechanism takes place because of the extremely strong nucleophilic property of water molecules, resulting in the ketone-based structure (Scheme 1 (B)). It seems that the degradation process happens along with the oxidation process of the copolymer chains. That is, the attack of water molecules takes place at the same time at which the first electron is removed from the co-polymer chains. This may be due to the slightly less aromaticity of selenophene in comparison with thiophene [68-69], which results in a higher reactivity in both electrophilic and nucleophilic aromatic substitution reactions. Moreover, the higher electrophilicity of the selenium atom also results in a greater tendency towards ring-opening reactions. Strong nucleophiles can attack at the selenium atom, which leads to ring-opening structure [70].

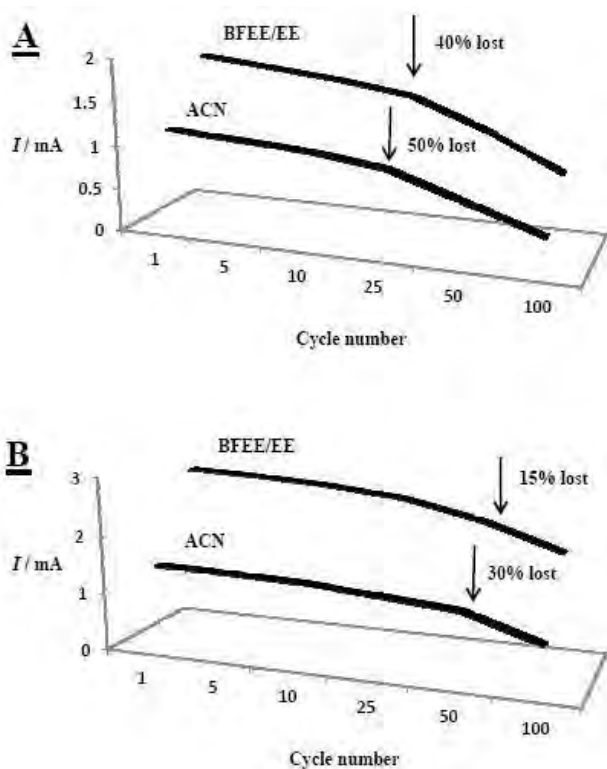


Fig. 9. Effect of polymerization medium on the electrochemical activity of polyselenophene (A) and copolymer (B) deposited at $E_{\text{SCE}} = 1.60$ V from solution containing Se: Th, mole ratio 1:1

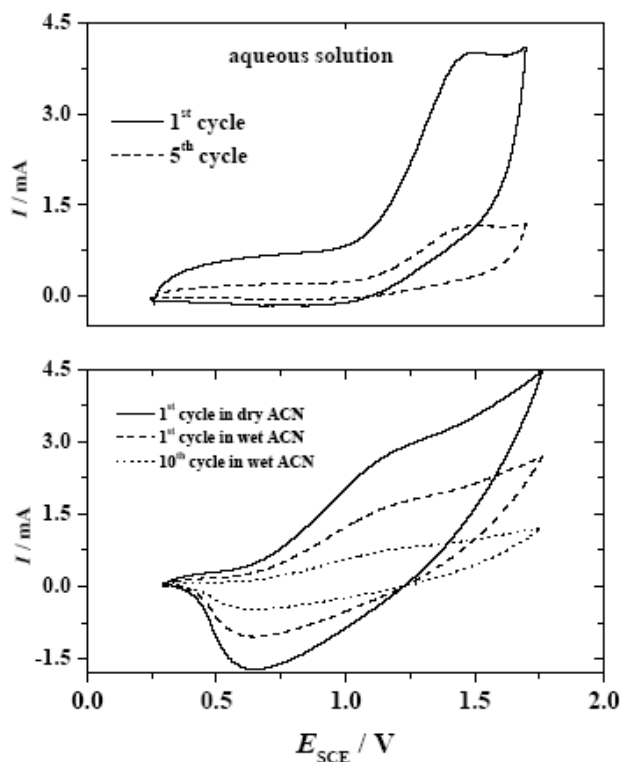
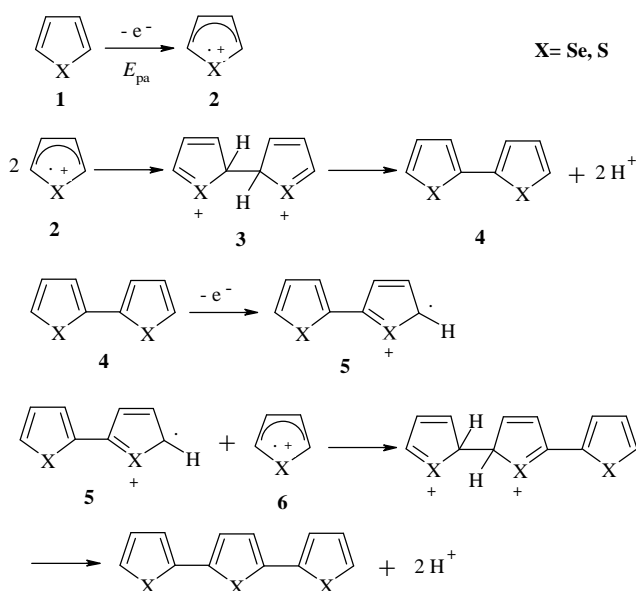


Fig. 10. CVs recorded in aqueous solution containing 0.10 M NaTFB and in acetonitrile/ H_2O (volume ratio 100:1)+ 0.10 M TBATFB solution of copolymer deposited at $E_{\text{SCE}} = 1.60$ V in a BFEE + EE (ratio 1:2) solution containing selenophene: thiophene, mole ratio 1:1; $dE/dt = 100$ mV/s

3.4. Proposed Mechanism of the Electrochemical Formation of Copolymer Films

The electropolymerization mechanism of copolymers is presumably even more complex than that of homopolymers [71]. Scheme 2 shows a proposed mechanism for the electropolymerization of selenophene and thiophene based on already known coupling reactions of aromatic compounds [72-74]. The first electrochemical step (E) is the oxidation of the monomer (1) into its radical cation. The second step involves the coupling of two radicals (2) to produce a dihydrodimer (3) dication that leads to a dimer (4) after the loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical step (C). At the applied electrode potential the dimer (4), which is more easily oxidized than the monomer, is present in its radical form (5) and undergoes further coupling with a monomeric radical (6). Electropolymerization then proceeds through successive electrochemical and chemical steps according to a general E(EC)_n mechanism until the oligomer becomes insoluble in the electrolyte solution and precipitates onto the electrode surface; soluble oligomers were observed to stray away from the electrode at the beginning of the polymerization.



Scheme 2. Proposed mechanism of the electropolymerization of selenophene-thiophene copolymers

3.5. FTIR Spectroscopy of Copolymer Films

The FTIR spectrum of the as prepared copolymer film (Fig. 11) showed α -CH and β -CH out of plane

bending at 756–924 cm^{-1} indicating that α - α' coupling of radical cations has taken place in the copolymerization. This is a characteristic of α -substituted five-membered heterocyclic compounds. C–H deformation in-plane bands at 1082–1220 cm^{-1} , aromatic ring stretches at 1372, 1446, 1531, and 1600 cm^{-1} representing that selenophene and thiophene rings remained intact after polymerization. The weak absorption around 1700 cm^{-1} and 1640 cm^{-1} corresponding to the C=O stretching vibration shows that some defects do exist in the polymer film.

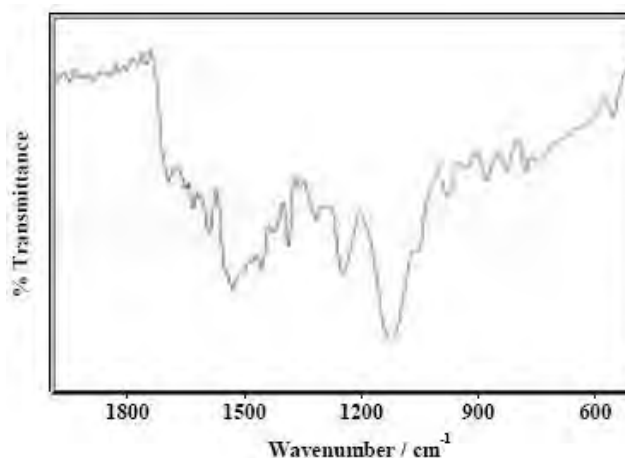


Fig. 11. FTIR spectra of copolymer deposited at $E_{\text{SCE}} = 1.60$ V in a BFEE + EE (ratio 1:2) solution containing selenophene: thiophene, mole ratio 1:1

It is noticed that the features of the FTIR spectra of the copolymer are between those of homopolymers previously published in the literature [28, 38, 44, 49] and cannot be explained by simple addition of the spectra of pure homopolymers. This may be due to the interaction between selenophene and thiophene monomer units in the copolymer chains, and may be regarded as evidence of copolymerization.

4. Conclusions

Electrochemical copolymerization of selenophene and thiophene was successfully performed in BFEE + EE (ratio 1:2) solution containing in addition 0.1 M TBATFB as supporting electrolyte at constant electrode potential. CVs of copolymer films show intermediate electrochemical properties between homopolymers. The homo- and copolymer films have only one redox peak caused by polymer oxidation and reduction. At higher polymerization potentials and at higher concentrations of thiophene in the feed more thiophene units are incorporated into the copolymer chain. The copolymer materials show fairly good stability of the redox activity in organic solvents. A mechanism for the electropoly-

merization of selenophene and thiophene based on already known coupling reactions of aromatic compounds has been proposed.

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References

- [1] Skotheim T. and Reynolds J. (Eds.): Handbook of Conducting Polymers, 3rd edn. CRC Press: Taylor & Francis Group, Boca Raton 2007.
- [2] Amanokura J., Suzuki Y., Imabayashi S. and Watanabe M.: J. Electrochem. Soc., 2001, **148**, D43.
- [3] Sotzing G., Briglin S., Grubbs R. and Lewis N.: Anal. Chem., 2000, **72**, 3181.
- [4] Lin C., Hwang B. and Lee C.: J. Appl. Polym. Sci., 1999, **73**, 2079.
- [5] Malinauskas A., Malinauskiene J. and Ramanavicius A.: Nanotechnol., 2005, **16**, R51.
- [6] James D., Scott S., Ali Z. and Ohare W.: Microchim. Acta, 2005, **149**, 1.
- [7] Guernion N and Hayes W.: Curr. Org. Chem., 2004, **8**, 637.
- [8] Vidal J., Garciaruiz E. and Castillo J.: Microchim. Acta, 2003, **143**, 93.
- [9] Dai L., Soundarrajan P. and Kim T.: Pure Appl. Chem., 2002, **74**, 1753.
- [10] Trojanowicz M., Velkrawczyk T. and Alexander P.: Chem. Anal., 1997, **42**, 199.
- [11] Trojanowicz M.: Microchim. Acta, 2003, **143**, 75.
- [12] Cosnier S.: Anal. Bioanal. Chem., 2003, **377**, 507.
- [13] Bartlett P. and Birkin P.: Synth. Met., 1993, **61**, 15.
- [14] Sadik O.: Electroanal., 1999, **11**, 839.
- [15] Wallace G., Smyth M. and Zhao H.: TRAC-Trend. Anal. Chem., 1999, **18**, 245.
- [16] Shinohara H., Aizawa M. and Shirakawa H.: J. Chem. Soc. Chem. Commun., 1986, 87.
- [17] Le H., Garcia B., Deslouis C. and Xuan Q.: J. Appl. Electrochem., 2002, **32**, 105.
- [18] Buckley L. and Eashoo M.: Synth. Met., 1996, **78**, 1.
- [19] Kelkar D. and Chourasia A.: Chem & Chem. Techn., 2011, **5**, 309.
- [20] Malinauskas A.: Synth. Met., 1999, **107**, 75.
- [21] Grundmeier G., Schmidt W. and Stretmann M.: Electrochim. Acta, 2000, **45**, 2515.
- [22] Gurunathan K., Mrurgan A., Marimuthu R. *et al.*: Mater. Chem. Phys., 1999, **61**, 173.
- [23] Otero T. and Cantero I.: J. Power Sources, 1999, **81**, 838.
- [24] Fritz B. and Paul R.: Electrochim. Acta, 2000, **45**, 2467.
- [25] Wallace G.: Trends Anal. Chem., 1999, **18**, 443.
- [26] Cosnier S.: *Biosen. Bioelectron.*, 1999, **14**, 443.
- [27] Parthasarathy R. and Martin C.: Nature, 1994, **369**, 298.
- [28] Xu J., Hou J., Zhang S. *et al.*: J. Electroanal. Chem., 2005, **587**, 345.
- [29] Bezoari M., Kovacic P., Gronowitz S. and Hornfeldt A.: J. Polym. Sci. Polym. Lett. Ed., 1981, **19**, 347.
- [30] Aqad E., Lakshmikantham M. and Cava M.: *Org. Lett.*, 2001, **3**, 4283.
- [31] Patra A. and Bendikov M.: J. Mater. Chem., 2010, **20**, 422.
- [32] Narita Y., Hagiri I., Takahashi N. and Takeda K.: Jpn. J. Appl. Phys., 2004, **43**, 4248.
- [33] Salzner U., Lagowski J., Pickup P. and Poirier R.: Synth. Met., 1998, **96**, 177.
- [34] Inoue S., Nakanishi H., Takimiya K. *et al.*: Synth. Met., 1997, **84**, 341.
- [35] Wang C., Ellern A., Becker J. and Bernstein J.: Adv. Mater., 1995, **7**, 644.
- [36] del del Valle M., Ugalde L., Diaz F. *et al.*: Polym. Bull., 2003, **51**, 55.
- [37] Sauvajol J., Chenouni D., Hasoon S. and Lere-Porte J.: Synth. Met., 1989, **28**, C293.
- [38] Glenis S., Ginley D. and Frank A.: J. Appl. Phys., 1987, **62**, 190.
- [39] Yoshino K., Kohno Y., Shiraishi T. *et al.*: Synth. Met., 1985, **10**, 319.
- [40] Groenendaal L., Zotti G., Aubert P. *et al.*: Adv. Mater., 2003, **15**, 855.
- [41] Tourillon G., Dartyge E., Guay D. *et al.*: J. Electrochem. Soc., 1990, **137**, 1827.
- [42] Jin S. and Xue G.: Macromolecules, 1997, **30**, 5753.
- [43] Shi G., Li C. and Liang Y.: Adv. Mater., 1999, **11**, 1145.
- [44] Pu S., Houb J., Xua J. *et al.*: Mat. Lett., 2005, **59**, 1061.
- [45] Huang W. and Park J.: J. Chem. Comm., 1987, 856.
- [46] Zotti G. and Gumbs R.: [in:] Nalwa H. (Ed.), Handbook of Organic Conductive Molecules and Polymers. Wiley, Chichester 1997, Ch. 5.
- [47] Alakhras F. and Holze R.: J. Appl. Polym. Sci., 2008, **107**, 1133.
- [48] Alakhras F. and Holze R.: Electrochim. Acta, 2007, **52**, 5896.
- [49] Alakhras F. and Holze R.: Synth. Met., 2007, **157**, 109.
- [50] Alakhras F. and Holze R.: J. Solid State Electrochem., 2008, **12**, 81.
- [51] Arjomandi J., Alakhras F., Al-Halasa W. and Holze R.: Jordan J. Chem., 2009, **4**, 279.
- [52] Pekmez N., Pekmez K., Holze R. and Yildiz A.: J. Appl. Polym. Sci., 2003, **89**, 862.
- [53] Ong T., Ng S. and Chan H.: Polymer, 2003, **44**, 5597.
- [54] Ng S., Chan H., Ong T. *et al.*: Macromolecules, 1998, **31**, 1221.
- [55] Kunugi Y., Takimiya K., Yamane K. *et al.*: Chem. Mater., 2003, **15**, 6.
- [56] Yamamoto T., Zhou Z., Kanbara T. *et al.*: J. Am. Chem. Soc., 1996, **118**, 10389.
- [57] Jenkins I., Salzner U. and Pickup P.: Chem. Mater., 1996, **8**, 2444.
- [58] Van Keuren E., Wakebe T., Andreaus R. *et al.*: Appl. Phys. Lett., 1999, **75**, 3312.
- [59] Alakhras F.: Mat. Sci., 2014, *in press*.
- [60] Li L., Chen W., Xu N. *et al.*: J. Mater. Sci., 2004, **39**, 2395.
- [61] Wan X., Zhang W., Jin S. *et al.*: J. Electroanal. Chem., 1999, **470**, 23.
- [62] Wan X., Yan F., Jin S. *et al.*: Chem. Mater., 1999, **11**, 2400.
- [63] Inzelt G., Pineri M., Schultze J. and Vorotyntsev M.: Electrochim. Acta, 2000, **45**, 2403.

- [64] Xu J., Shi G., Xu Z. *et al.*: J. Electroanal. Chem., 2001, **514**, 16.
[65] Shreepathi S. and Holze R.: Chem. Mater., 2005, **17**, 4078.
[66] Can M., Pekmez K., Pekmez N. and Yildiz A.: J. Appl. Polym. Sci., 2000, **77**, 312.
[67] Wan X., Li L., He J. *et al.*: J. Appl. Polym. Sci., 2002, **86**, 3160.
[68] Fringuelli F., Marino G., Taticchi A. and Grandolini G.: J. Chem. Soc., Perkin Trans., 1974, **2**, 332.
[69] Cyranski M., Krygowski T., Katritzky A. and Schleyer P.: J. Org. Chem., 2002, **67**, 1333.
[70] Gronowitz S., Hallberg A. and Frejd T.: Tetrahedron, 1979, **35**, 2607.
[71] Roncali J.: Chem. Rev., 1992, **92**, 711.
[72] Asavapiriyonont S., Chandler G., Gunawardena G. and Pletcher D.: J. Electroanal. Chem., 1984, **177**, 229.
[73] Genies E., Bidan G. and Diaz A.: J. Electroanal. Chem., 1983, **149**, 113.
[74] Pinzino C., Angelone R., Benvenuti F. *et al.*: J. Polym. Chem., Polym. Phys., 1986, **36**, 1901.

ЕЛЕКТРОСИНТЕЗ ПОЛІ(СЕЛЕНОФЕН-КО- ТІОФЕНОВИХ) ПЛІВОК В ДИЕТИЛТЕРАТІ ТРИФЛУОРИСТОГО БОРУ/ЕТИЛОВОМУ ЕТЕРІ

Анотація. Проведено електросинтез селенофен-тіофен кополімерів при постійному електродному потенціалі в бінарній системі розчинників, що складається з диетилтерату трифлуористого бору і додатковою кількістю етилового етеру (мольне співвідношення 1:2). Отримано гомо-і кополімерні плівки, які охарактеризовані за допомогою циклічної вольтамперометрії та ІК-Фур'є спектроскопії. Досліджено вплив зовнішнього потенціалу полімеризації і співвідношення селенофен/тіофен. Показано, що отримані плівки стабільні в окиснювально-відновній активності в розчині електроліту на основі ацетонітрилу.

Ключові слова: електрополімеризація, провідні кополімери, політіофен, поліселенофен, циклічна вольтамперометрія.