

ELECTROCHEMICAL SYNTHESIS OF 3-METHYLTHIOPHENE/3,4-ETHYLENEDIOXYTHIOPHENE COPOLYMERS AND THEIR ELECTROCHROMIC PROPERTIES

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3-methylthiophene / 3,4-ethylenedioxythiophene (3MT/EDOT) copolymer have been synthesized by electrochemical polymerization (electrodeposition) on transparent ITO glass electrodes from the joint monomer solutions at the 3MT:EDOT feed ratios: 9999:1, 9990:10, 9900:100, 9000:1000. The copolymer nature of the electrodeposited films has been proved by investigations of their spectral, electrochemical, spectroelectrochemical and electrochromic properties. It has been found that although the copolymers obtained from solutions with small contents of EDOT have spectral properties quite similar to those of the pure poly(3-methylthiophene) P3MT their electrochromic behavior is significantly improved due to much less switching times.

Research methodology

Materials and preparations

Monomers 3-methylthiophene (3MT, Merck), 3,4-ethylenedioxythiophene (EDOT, Aldrich), background electrolyte LiClO₄ and solvent acetonitrile (Merck) were of reagent grade and used as received. Dry electrolyte solutions of the monomers in 0.1 M LiClO₄ in acetonitrile were prepared from the thoroughly dried components in a dry glove-box under a nitrogen atmosphere.

Electrochemical polymerization and cyclic voltammetry

The electrochemical syntheses (electrodeposition) of the pure polymers and copolymers were carried out on the transparent conductive indium tin oxide (ITO) covered glass substrates in a sealed cell using 0.1M solution of LiClO₄ in acetonitrile as a background electrolyte solution in potentiostatic mode at 1.3 V. The total concentration of 3MT and EDOT monomers in the solution was 0.05 M with the feed ratios: 9999:1, 9990:10, 9900:100, 9000:1000.

Cyclic voltammograms (CVs) were recorded at a scan rate of 50 mV/s in the potential range from -700 mV to 900 mV. Background

currents at the electrochemical polymerization potentials did not exceed 0.01 mA/cm².

All electrochemical experiments were performed with the help of the potentiostat IPC-Pro. Potentials were measured versus Ag/Ag⁺ (Ag / (0.1 M AgNO₃ + 0.1 M LiClO₄ in acetonitrile) reference electrode

Spectral and electrochromic measurements

Spectral and spectroelectrochemical studies of the polymers were carried out in a sealed three-electrode cell based on an optical glass cuvette. The cell was mounted perpendicularly to the light beam of the spectrophotometer Carry 50 (Varian) while its electrodes were connected with the potentiostat. This configuration of the spectroelectrochemical system allowed running electrochemical polarization (-500 ÷ 800 mV) of the ITO electrodes covered by the polymers simultaneously with registration of their UV-Vis spectra. Scanning of the spectra was carried out at a rate of 400 nm/sec after keeping the polymer at the given potential for 10 sec. The spectra were recorded in the range from 300 to 1100 nm.

Diagrams of switching time of the electrodeposited (co)polymer films under electrochemical polarization were built with the help of the described spectroelectrochemical system. The spectral characteristics of the samples of polymers and copolymers were recorded under polarization at a fixed wavelength of 480 nm with spectral scan-rate of 2ms⁻¹. The exposure time for a given potential is 20 s. The potentials were switched sharply between -500 mV and 800 mV

Results and Discussion

Electrochemical synthesis and behavior of the copolymers

As one can see from CVs of the individual monomers, oxidation of EDOT and, therefore, its polymerization process starts by 400mV earlier than that of 3MT (Fig. 1, curves 6 and 1). This difference can be explained by both a strong electron donating effect of the ether groups at the β, β-positions of thiophene ring and preventing the formation of parasitic α-β linkages during polymerization [5], which in turn allows obtaining a more regular structure of PEDOT in comparison with poly(3-alkylthiophenes) [6]. As a consequence, in the case of co-oxidation of EDOT and 3MT, an obvious decrease in the potential of the beginning of the electrochemical process with an increase of the amount of EDOT in the feed ratio is observed (Fig. 1). Inevitably decreasing the initial electrochemical polymerization potentials allows obtaining the more stable polymer [5,7].

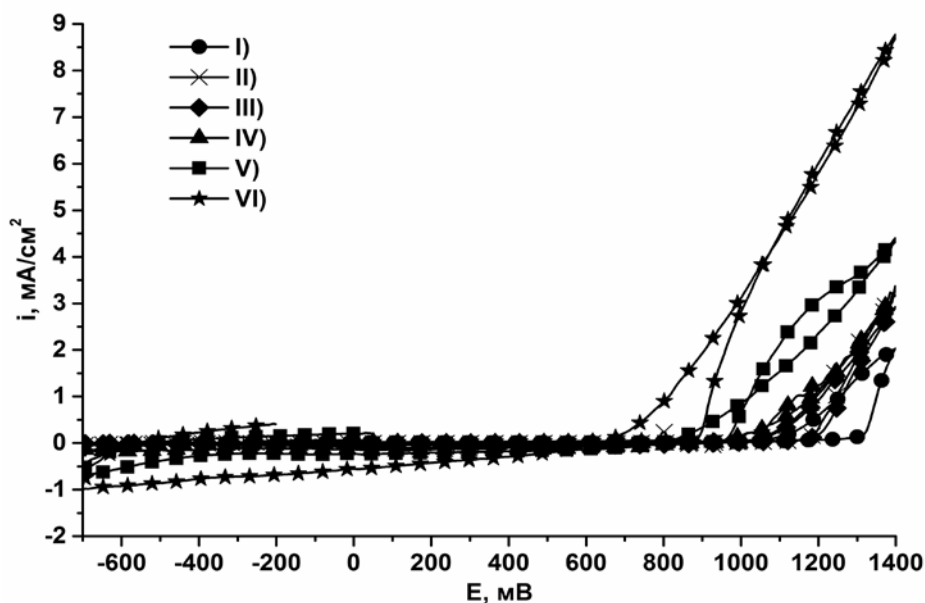


Fig. 1. First cycle of the electrochemical polymerization process of 3MT, EDOT and their mixture: I – 3MT, II - 3MT:EDOT = 9999:1, III- 9990:10, IV - 3MT:EDOT = 9900:100, V - 9000:1000, VI - EDOT

Importantly, the changes in the shape of the CVs of the polymer films on ITO electrodes are symbatic to the growth of the ratio of EDOT/3MT (Fig. 2). Indeed, the films obtained from solutions with a small amount of EDOT (feed ratios 3MT:EDOT = 9999:1, 9990:10) demonstrate CVs identical to those of poly(3-methylthiophene) (P3MT) with small peak shift from 580mV to 510-530mV, respectively. However, after increasing the EDOT amount (for the feed ratio 3MT:EDOT = 9900:100) the characteristic peak on the anode branch shifts to the more negative potentials 380-390 mV. These changes suggest facilitation of the electrochemical oxidation of the electrodeposited polymer films due to increasing content of EDOT moities in the macromolecular chains that strongly indicates formation of real EDOT/3MT copolymers instead of the simple PEDOT/P3MT mixture. Polymer layers synthetized from the polymerization mixture with the ratio 3MT:EDOT equal to 9000:1000 demonstrate electrochemical properties close to that of PEDOT.

Spectral studies of copolymers

UV-Vis spectra of the films electrodeposited on ITO (Fig.3) confirm the formation of the 3MT/EDOT copolymers in the course of the electrochemical polymerization in the joint solutions of both monomers.

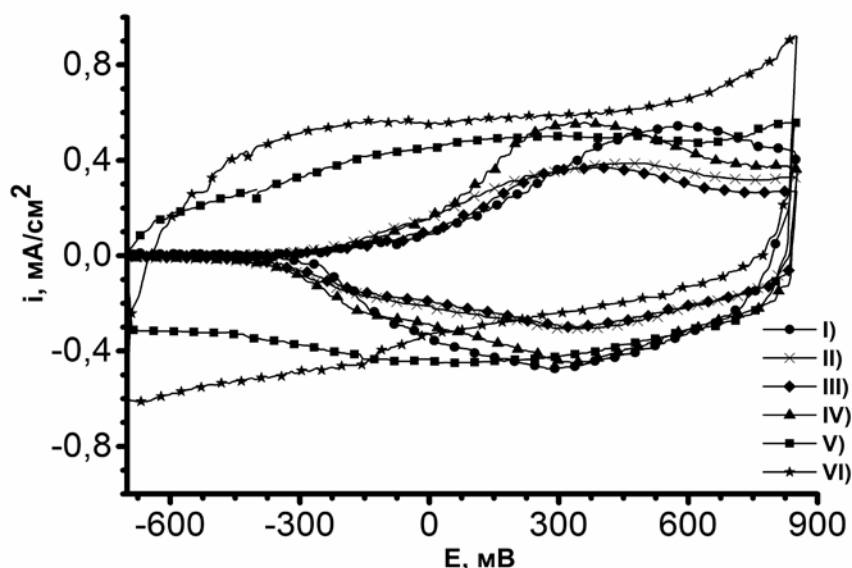


Fig. 2. CVs of polymer layers obtained from polymerization mixture with different ratio of 3MT:EDOT: I – 3MT, II - 3MT:EDOT = 9999:1, III- 9990:10, IV - 3MT:EDOT = 9900:100, V - 9000:1000, VI - EDOT

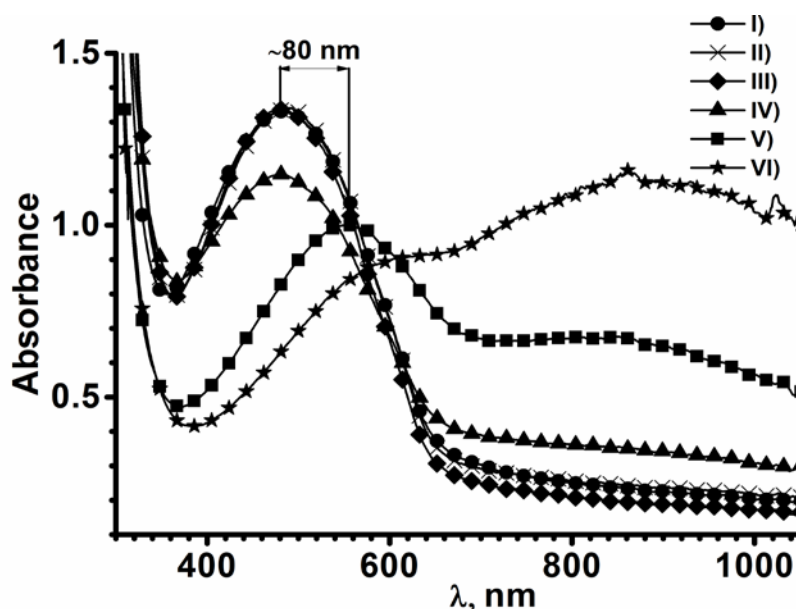


Fig. 3. UV-Vis spectra of reduced form of the polymer layers obtained from polymerization mixture with different ratio of 3MT:EDOT: I – 3MT, II - 3MT:EDOT = 9999:1, III- 9990:10, IV - 3MT:EDOT = 9900:100, V - 9000:1000, VI - EDOT

Specifically, while UV-Vis spectra of the films electrodeposited from polymerization mixture with feed ratios 3MT:EDOT = 9999:1, 9990:10, 9900:100 demonstrate only weak quantitative differences from the spectrum of P3MT film, these changes, nevertheless, are enhanced with the EDOT contents in the ratio (e.g. height of the P3MT peak at 480 nm and absorption in red and infrared regions of the spectra II, III and IV in Fig.3). Moreover, at higher EDOT contents in the system (3MT:EDOT = 9000:1000) one can see also quantitative differences in the spectra

namely characteristic peak of P3MT strongly decreases and shifts to 560 nm (Fig.3, spectrum V). A strong growth of absorption in the near infrared region of this spectrum suggests not only enhanced conductivity of this electrodeposited film but also a significant increase of EDOT links in the macromolecular chains of formed copolymer as compared with other ones. This suggestion agrees well with the pure PEDOT spectrum

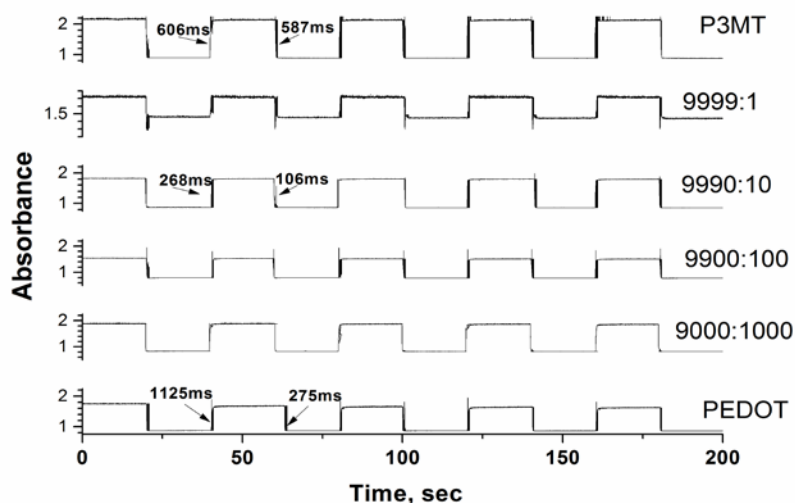


Fig. 4. Time plots of the electrodeposited pure polymers and copolymers films at 480nm during repeated switching between their bleached (at -500 mV) and coloured (at 800 mV) states.

Electrochromic behavior of the copolymers

Spectroelectrochemical studies and electrochromic behavior of the electrodeposited films demonstrated that spectral transitions at different potentials and coloration in the case of the copolymers with feed ratios 9999:1, 9990:10, 9900:100 were almost similar to those of the pure P3MT. However, the copolymer obtained with the feed ratio 9000:1000 acquired the colors inherent for PEDOT. Nevertheless, as one can see from Fig. 4, there is a quite strong dependence of switching time between their bleached (at -500 mV) and colored (at 800 mV) states the feed 3MT: EDOT ratio in the polymerization solution.

In particular, the switching times for the pure P3MT were 606 ms and 587 ms for switch from reduced to oxidized and from oxidized to reduced form, respectively, while in the case of the pure PEDOT these values were 1125 ms and 275 ms, respectively. In the copolymers the switching times were strongly different. Surprisingly, that minimal switching times were found for the copolymer the smallest ratio 3MT:EDOT=9990:10 namely 268ms and 106ms, respectively.

Conclusions

An investigation of the 3MT/EDOT copolymers synthesized from polymerization mixtures with different feed ratios of 3MT:EDOT has

demonstrated that spectral, electrochemical, spectroelectrochemical and electrochromic properties of the copolymers change with EDOT content. Specifically, the copolymer films electrodeposited from the polymerization mixtures with small contents of EDOT have properties quite similar to those of the pure P3MT. Significant changes in these spectral properties were observed in the copolymers obtained from polymerization mixture with EDOT a concentration higher than 1%. Electrochromic properties of the 3MT-EDOT copolymers were characterized by measuring the switching times. It is found that minimal switching times are characteristic for the copolymer film electrodeposited from the solution with the feed ratio of 3MT:EDOT=9990:10.

Based on results of this study one can deduce that using even small 3MT:EDOT feed ratios in the polymerization mixture allows to synthesize 3MT/EDOT copolymers with spectral properties close to those of P3MT but with significantly improved electrochromic ability due to much less switching times.

References

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