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Copolymer electrosynthesis of ethyl-3-thiophene acetate and 3-methylthiophene and characterization of the resulting copolymers by spectroscopic studies

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Abstract Copolymers of ethyl-3-thiophene acetate (ETA) and 3-methylthiophene (MT) were synthesized electrochemically. Electrospray ionization mass spectra of the electrolyte containing 2×10^{-3} M MT + 3×10^{-2} M ETA after copolymerization showed cooligomers with different combination of ETA and MT units. Just one value of the glass transition temperature was observed by differential scanning calorimetry of the formation of homogeneous copolymers. Change of the copolymer composition led to change of thermal stability characterized by thermogravimetric analysis. The morphology of the copolymer film was studied by scanning electron microscopy, indicating a homogeneous and compact film. The electroactivity of the homopolymer/copolymer films was studied. Cyclic voltammograms of the polymer films revealed that poly(ethyl-3-thiophene acetate) possesses high electroactivity in non-aqueous solution, but its electroactivity was lost entirely after 50 cycles in 0.1 M $N(\text{Bu})_4\text{PF}_6$ /acetonitrile solution having 5 volume percentage of water; however, the copolymer of ETA and MT maintains its high electroactivity even in the aqueous solution. Similar results were also derived from impedance and photoelectrochemical measurements. Additionally, it was found that a bilayer of poly(3-methylthiophene) and copolymer was formed.

Keywords Copolymer · Organic semiconductor · Mass spectroscopy · Photoelectrochemistry · Electrochemical impedance spectroscopy

Introduction

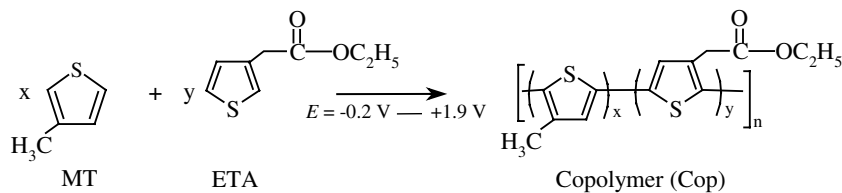
Electrochemical polymerization of heterocyclic monomers leading to corresponding electroactive and conductive polymers is of interest in both basic research and technological applications because of the interesting optical and electrical properties as well as the stability of the polymers [1, 2]. Among these polymers, the functionalized conducting polymers have received particular attention, because they possess two interesting functions, a specific functional group on the surface and an extended π -conjugation system. The first function is employed for modification of the polymer surface by immobilization of biomolecules, generating new materials for application in amperometric biosensors [3–5] and electrocatalysis [6]. These enzyme electrodes facilitate the electron transfer between the active centers of enzymes and the electrode through the polymer film [7]. Thus, the second function would play an important role as a charge-transfer mediator. Nevertheless, the extended π -conjugation and the desirable electroactivity of functionalized polymer chains could not be achieved due to steric and electronic influence of the functional group [8].

A big step forward to the development of conducting polymers is the electrochemical copolymerization of simple and functionalized thiophenes bearing ester groups with non-substituted thiophenes. Many investigations of this approach have been described [9, 10]. The obtained copolymers possess high electroactivity comparable with that of non-substituted polythiophenes in non-aqueous solution. Confirmation of the copolymer formation was based on analytical data of electrochemistry and IR spectroscopy. In the current work, similar copolymerization was studied, but the research was concentrated on an investigation of the electroactivity of the films in both aqueous and non-aqueous solutions, and the structure of the resulting copolymers.

In this paper, the electrochemical copolymerization of ethyl-3-thiophene acetate and 3-methylthiophene was

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Scheme 1 Electrochemical copolymerization of 3-methylthiophene (MT) and ethyl-3-thiophene acetate (ETA)



examined, as shown schematically in Scheme 1. By using a variety of techniques, such as cyclic voltammetry, ESI mass spectroscopy, thermal analysis, and photocurrent and impedance spectroscopy, evidence for the copolymer formation as well as the structure of the resulting copolymer film was achieved.

Experimental details

Chemicals

Ethyl-3-thiophene acetate and 3-methylthiophene (Aldrich) were synthetically graded and used as received. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($\text{N}(\text{Bu})_4\text{PF}_6$, Aldrich) in acetonitrile (Fischer, 999 % for DNA analysis), if not stated otherwise. Methanol (Aldrich, 999% for capillary-GC) was used for spectroscopic measurements and lithium perchlorate (LiClO_4 , Fluka, p.a., <0.2 % water) was used as received.

Apparatus and procedure

Electrochemical copolymerization and characterization were performed in a conventional three-electrode cell by cyclic voltammetry in the potential range of -0.20 to 1.90 V. Platinum working (area 1 cm^2) and counter (area 3.14 cm^2) electrodes were used. A saturated calomel electrode (SCE, $E = 0.24$ V vs. normal hydrogen electrode) was the reference electrode (all potentials mentioned in this paper were related to SCE). In order to prevent water diffusion from the reference electrode into the working electrolyte, a salt bridge was used. The electrochemical behavior of the obtained copolymer films was characterized in the monomer-free electrolyte after rinsing with acetonitrile to remove residual monomers and oligomers. To reach stable conditions, the films were cycled in the potential range from -0.20 to $+1.40$ V at a scan rate of 50 mV/s . This potential range covers the redox potentials of the two homopolymers. A potentiostat/galvanostat EG&G model 263A was used for the electrochemical measurements.

After copolymerization, the electrolyte was investigated by electrospray ionization (ESI) mass spectroscopy (Hewlett-Packard-Bruker ESQUIRE LC-MS), using 0.5 M ammonium acetate in methanol as solvent. To avoid very strong signals coming from the supporting electrolyte (0.1 M $\text{N}(\text{Bu})_4\text{PF}_6$), measurements were made with 0.1 M LiClO_4 .

For thermal analysis and infrared (IR) spectroscopy, the polymer films were peeled off the electrode, and then washed with methanol in a soxhlet extractor for 5 h in order to remove residual monomers and supporting electrolyte. Differential scanning calorimetry (DSC) was made with a METTLER DSC 30, operating at a heating rate of 5 K min^{-1} under N_2 atmosphere. An empty aluminum pan was used as reference. Thermogravimetric analysis (TGA) was performed on a METTLER TG 50 thermal analyzer, operating at 10 K min^{-1} under N_2 atmosphere. Infrared spectra of copolymer/KBr sample were recorded with a Nicolet 800-FTIR spectrometer.

Photoelectrochemical (PEC) spectra were registered in a three-electrode cell with an optical window. A $1,000 \text{ W}$ Xenon lamp was employed as a light source in combination with a grating monochromator (Zeiss, M4QIII) and a light chopper (PAR 197) at a frequency of 400 Hz . In order to polarize the polymer-modified electrode, a potentiostat/galvanostat HEKA model D 6734 was used. The photocurrent signal was registered with a PAR model 5208 lock-in amplifier.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the monomer-free electrolyte, using a Zahner-Elektrik IM6d impedance measurement system. An a.c. amplitude of 10 mV was applied and the data was taken in the frequency range of 0.1 Hz to 100 kHz . The polymer film was polarized in the reduced form at 0.00 V for 1 h, and then the potential was changed in the anodic direction in steps of 50 mV . The EIS measurements were made after an equilibration time of 12 min at each applied potential.

The morphology of the polymer films was characterized by scanning electron microscopy (ZEISS DSM 982 Gemini).

Results and discussion

Synthesis of copolymer films

Copolymers were synthesized from the 0.1 M $\text{N}(\text{Bu})_4\text{PF}_6$ /acetonitrile solution having monomer ratios $[\text{MT}]/[\text{ETA}]$ of 1/1, 1/15, and 1/30, abbreviated as Cop1/1, Cop1/15, and Cop1/30, respectively.

In order to determine the optimal conditions for copolymerization, the oxidation potentials of MT ($E_{\text{ox}} = +1.55 \text{ V}$) and ETA ($E_{\text{it ox}} = +1.70 \text{ V}$) were determined by cyclic voltammetry. Figure 1 illustrates the dynamic process of polymerization in the potential range from -0.20 V to $+1.90 \text{ V}$. The redox potential waves are typical characteristics for polythiophenes. In

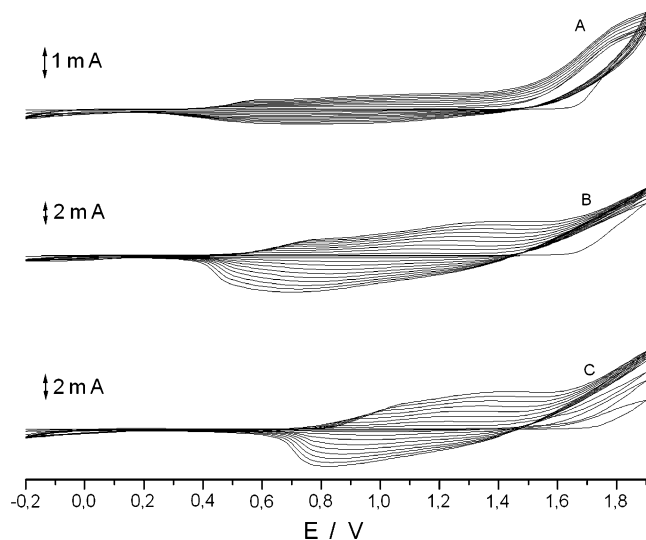


Fig. 1 Polymerization by cyclic voltammetry (CVs) in the 0.1 M $\text{Bu}_4\text{NPF}_6/\text{acetonitrile}$ solution containing 2×10^{-3} M MT (a), 2×10^{-3} M MT + 3×10^{-2} M ETA (b) and 3×10^{-2} M ETA (c), 50 mV/s

the anodic scan, the oxidation wave was found in the range of +0.40 to +1.40 V for poly(3-methylthiophene) (PMT) (*curves a*) and +0.80 to +1.60 V for poly(ethyl-3-thiophene acetate) (PETA) (*curves c*), whereas this wave was found from +0.55 to +1.60 V for Cop1/15 (*curves b*). Corresponding reduction waves were also observed in the cathodic scan. The redox peaks of the copolymers contain elements of corresponding homopolymers, implying that the coupling reactions between two radical cations of MT and ETA occurred to generate reactive copolymer chains.

The increase of the charge during polymerization and copolymerization with the number of cycles is shown in Fig. 2. It is remarkable that the charge value for the copolymers is larger than that for the homopolymers. The charge of Cop1/15 is similar to that of PMT, indicating that the MT content in the copolymer film is dominant. The charge value of Cop1/30 is roughly the sum of that of PETA and PMT.

Electrochemical characterization of the resulting homopolymer/copolymer films was carried out in the monomer-free 0.1 M $\text{N}(\text{Bu})_4\text{PF}_6/\text{acetonitrile}$ solution as shown in Fig. 3. The oxidation potential of the copolymer film shifts from +0.40 V for Cop1/15 (*curve b*) to +0.52 V for Cop1/30 (*curve c*). The oxidation potentials for PMT and PETA are +0.20 V and +0.85 V, respectively. The broadening of the oxidation peaks of Cop1/15 and Cop1/30 compared with that of homopolymers can be attributed to the variety of the redox sites and their interaction within the copolymer [11]. This result confirms the copolymer formation. The typical shoulders at potentials of +0.35 V for PMT, +0.59 V for Cop1/15, +0.75 V for Cop1/30 and +1.05 V for PETA are assigned to conformational changes in the geometry of the polythiophene backbone

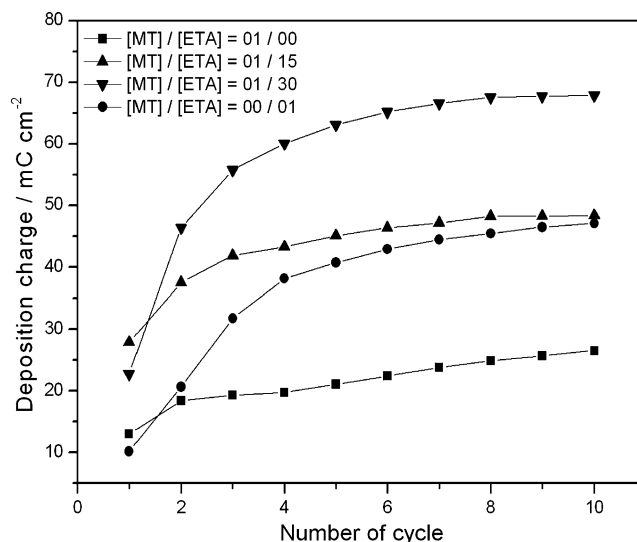


Fig. 2 The dependence of the charge during polymerization and copolymerization of MT and ETA on the number of cycles, 50 mV/s

during doping–undoping [8] or to different conjugation lengths [12, 13].

IR spectroscopy

The incorporation of ester groups in the copolymer films was demonstrated by IR measurements. The characteristic absorption band at $1,732 \text{ cm}^{-1}$ is assigned to the carbonyl group in the copolymer. This absorption band corresponds to that of the corresponding monomer, ETA. It indicates that the ester group is not damaged during the copolymerization process. It should also be mentioned that the ester group was used as a precursor

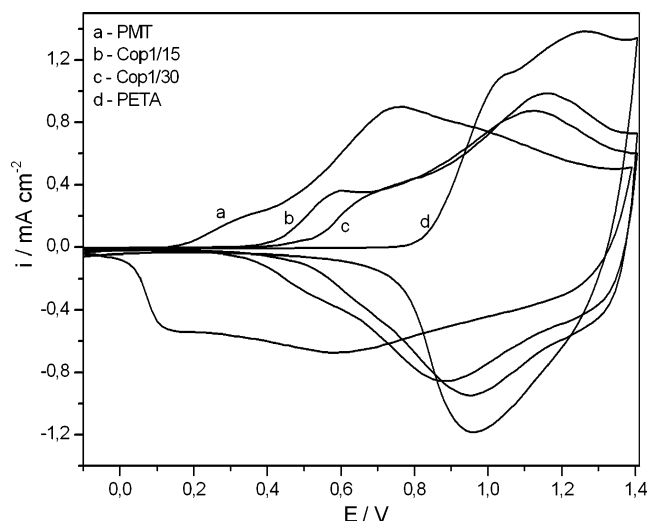


Fig. 3 CVs of homopolymer/copolymer films in monomer-free M $\text{N}(\text{Bu})_4\text{PF}_6/\text{acetonitrile}$ solution, 50 mV/s

group to immobilize biomolecules on the polymer surface [14].

ESI mass spectroscopy

When considering nucleation and growth of conducting polymers described in the literature [15, 16], the question is: it is possible to form a true copolymer from a mixture of monomers. This can be studied by an analysis of the residual electrolyte after copolymerization. The experiment was done in the 0.1 M LiClO₄/acetonitrile solution containing 2–10⁻³ M MT + 3 10⁻² M ETA after copolymerization in the potential range of -0.20 V to +1.90 V for 20 min. The electrolyte was analyzed by ESI mass spectroscopy. As expected, peaks originating from cooligomers with different combinations of MT and ETA units (MT_xETA_y) could be found. The assignment of some typical peaks is summarized in Table 1. Besides homooligomers MT₆ (m/z = 601.7) and ETA₃ (m/z = 524.5), a variety of statistically mixed cooligomers was found. It can be concluded that the electrochemical copolymerization produces a true copolymer.

Thermal analysis

Differential Scanning Calorimetry measurements of the homopolymers/copolymers were performed in the heating range from 30 °C to 140 °C. The obtained results indicate that no first-order phase transition such as melting and crystallization occurs. One clear second-order glass transition (*T_g*) was observed at 69.8 °C for Cop1/15 and 76.9 °C for Cop1/30, indicating that the copolymer formed one homogeneous phase. The value *T_g* of the copolymers increased from PETA (56.7 °C) to PMT (83.4 °C) with decreasing ETA content in the copolymer film, suggesting that the value of *T_g* is dependent on the copolymer composition. The result also showed that PETA is a low-*T_g* polymer in comparison

Table 1 Values of some typical peaks and their assignments in ESI mass spectroscopy of 0.1 M LiClO₄/acetonitrile solution containing 2×10⁻³ M MT + 3×10⁻² M ETA after copolymerization, *E* = -0.20 V - +1.90 V for 20 min

Value	Assignment	Exact m/z
289.0	MT ₁ ETA ₁ Na ⁺	289.0
369.0	MT ₂ ETA ₁ Li ⁺	369.1
451.0	MT ₁ ETA ₂ NH ₄ ⁺	452.0
524.5	ETA ₃ NH ₄ ⁺	524.1
601.7	MT ₆ Na ⁺	601.1
763.7	MT ₆ ETA ₁ NH ₄ ⁺	764.0
828.1	MT ₅ ETA ₂ 2H ⁺ Li ⁺	828.1
907.6	MT ₄ ETA ₃ NH ₄ ⁺	908.0
988.9	MT ₅ ETA ₃ 3H ⁺	989.1
1072.9	MT ₃ ETA ₅ K ⁺	1073.1
1150.6	MT ₁₀ ETA ₁ NH ₄ ⁺	1150.2

with non-substituted polythiophenes, due to the higher mobility of polymer chain [17].

The thermal stability of the homopolymers/copolymers was investigated by TGA. The TGA curve of the copolymers is positioned between those of the corresponding homopolymers and is dependent on the copolymer composition. This is a further proof of copolymer formation [18]. The thermal stability of PETA is lower than that of PMT. The thermal stability of the copolymer increased remarkably when increasing the MT content in the copolymers.

SEM Micrographs

Figure 4c displays the morphology of Cop1/15 film. For comparison, the morphology of PMT and PETA films are shown in Figs. 4a and b, respectively. It is also noticed that the morphological structure of functional polymer PETA is quite porous and inhomogeneous (Fig. 4b), whereas PMT film has a very compact and highly ordered structure.

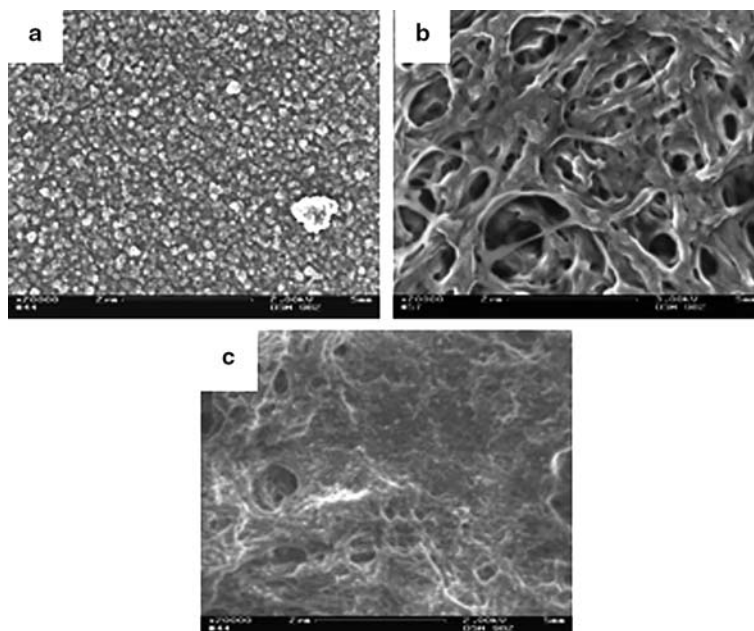
Electroactivity of the poly(ethyl-3-thiophene acetate) and its copolymer films

The PETA film was characterized in the monomer-free 0.1 M N(Bu)₄PF₆/acetonitrile solution. It can be seen that the PETA film is quite stable under these experimental conditions. The CVs of the PETA film were nearly unchanged after 50 cycles as shown in Fig. 5. The ratio of the charges for oxidation and reduction was close to one, indicating that the PETA is a highly electroactive polymer. The same behavior was also observed for the copolymer and PMT films.

When water was added to the working electrolyte (approximately 5 volume percentage of water), the electroactivity of the pure PETA film was lost after 50 cycles, as shown in Fig. 6. This is explained by the rapid nucleophilic attack of water molecules on positive charge centers of the polymer chains, i.e. polarons and bipolarons [19]. This leads to a change of the coplanar π-conjugation. The electroactivity of the film can also be lost as a result of the steric hindrance of the bulky substituents to the formation of extended π-conjugated polymer backbones [8]. No such phenomenon was observed for the PMT film under same conditions. The CVs revealed that pure PMT film is a high electroactive material even in aqueous solutions.

Fig. 7 shows CVs of the copolymer film Cop1/1 in the electrolyte containing 5 volume percentage of water. The potential was scanned in this experiment to only +1.20 V, because of the loss of electroactivity of pure PETA films in the same electrolyte (Fig. 6). The electroactivity of the copolymer film Cop1/1 decreased significantly during the 140 cycles, but the decomposition of the polymer occurred much slower, compared to the homopolymer PETA. The decrease in electroactivity

Fig. 4 Micrographs of homopolymer/copolymer films
a PMT, **b**PETA and
 copolymer Cop1/15



was faster in the electrolyte containing 30 volume percentage of water. The CVs also indicated that the electroactivity of the films with higher ETA contents decreased faster. In contrast to these results, no significant loss in electroactivity was observable in water-free electrolyte.

Impedance measurement

Figure. 8 illustrates the impedance spectra of PETA film in the electrolyte at various applied potentials from +0.60 V to +1.20 V, covering the redox waves of the PETA film. It was found that just one time constant

(RC) was observed in the whole frequency range. The decrease in resistance involving the doping process of the PETA film was observed on increasing the applied potential from +0.60 V (undoped state) to +1.20 V (doped state), whereas the corresponding capacitance increased as marked in Fig. 8.

Figure. 9 displays impedance spectra of the resultant copolymer film Cop1/15 in the potential range covering the redox potentials of the corresponding polymers. Unlike the impedance spectra of the pure PETA film, two time constants were found. The time constant in the low-frequency range can be assigned to capacitance and corresponding resistance of thin PMT layer (region I). The high-frequency response of the system consisting of

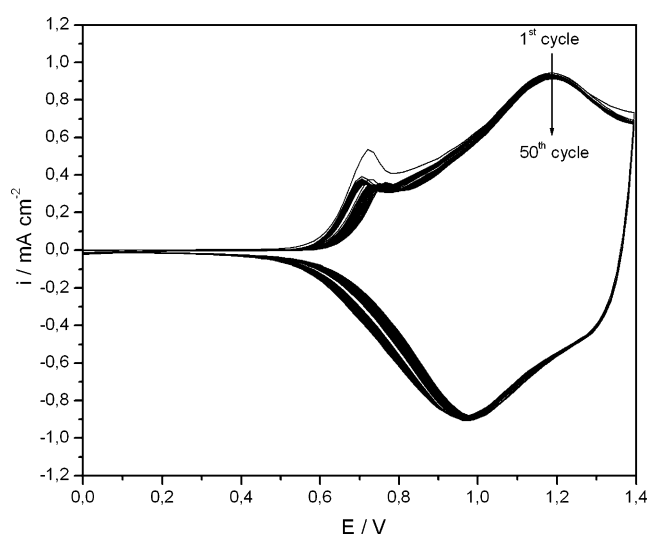


Fig. 5 Stability test: CVs of PETA films in the monomer-free 0.1 M $N(Bu)_4PF_6$ /acetonitrile solution, 50 mV/s

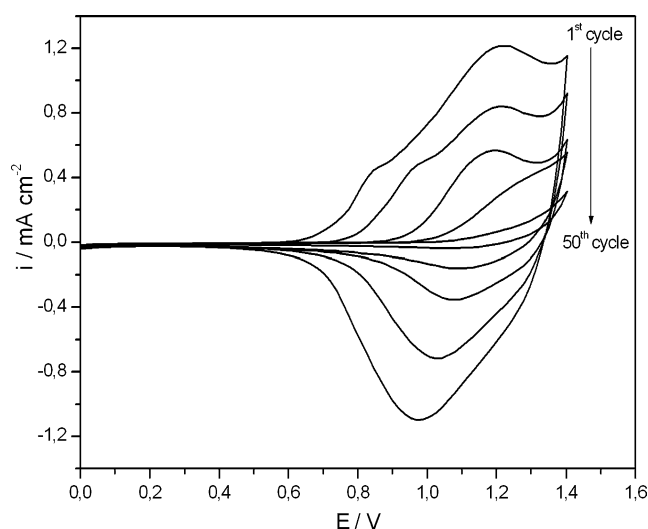


Fig. 6 Stability test: CVs of PETA films in monomer-free $M N(Bu)_4PF_6 + 5\% H_2O$ acetonitrile solution, 50 mV/s (every tenth cycle was recorded)

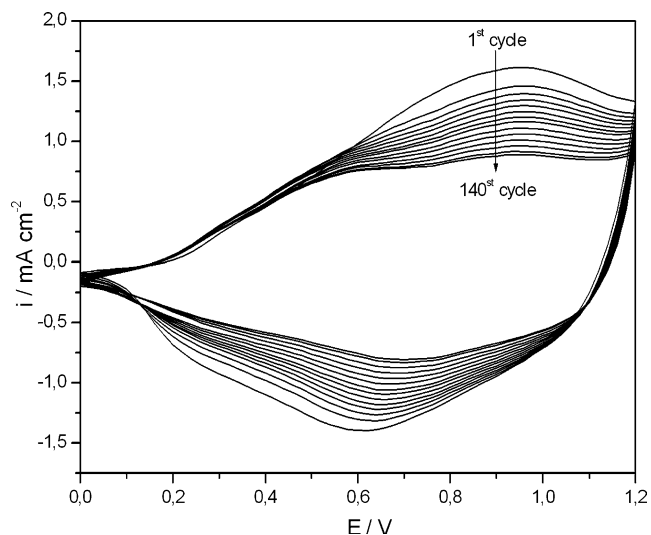


Fig. 7 Stability test: CVs of Cop1/1 films in monomer-free 0.1 M $N(\text{Bu})_4\text{PF}_6 + 5\% \text{H}_2\text{O}$ acetonitrile solution, 50 mV/s (every tenth cycle was recorded)

Fig. 8 Bode plots of PETA film at different applied potentials (*solid lines*) modulus of impedance and (*dotted lines*) phase shift, recorded in 0.1 M $N(\text{Bu})_4\text{PF}_6/\text{acetonitrile}$ solution

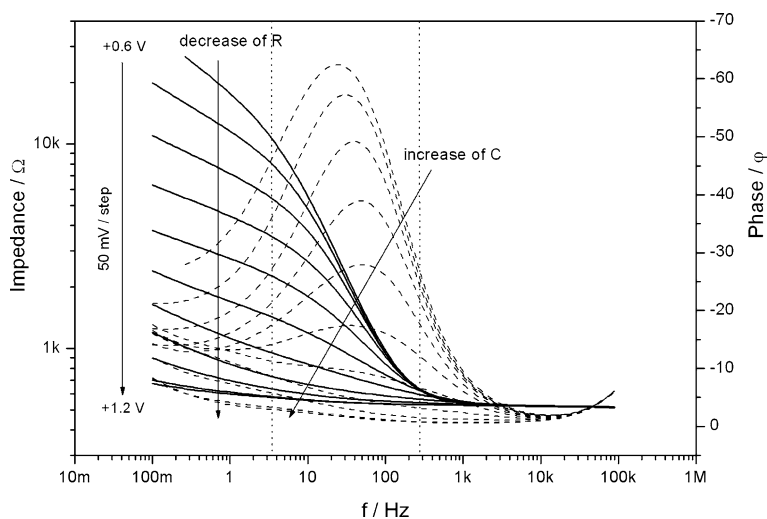
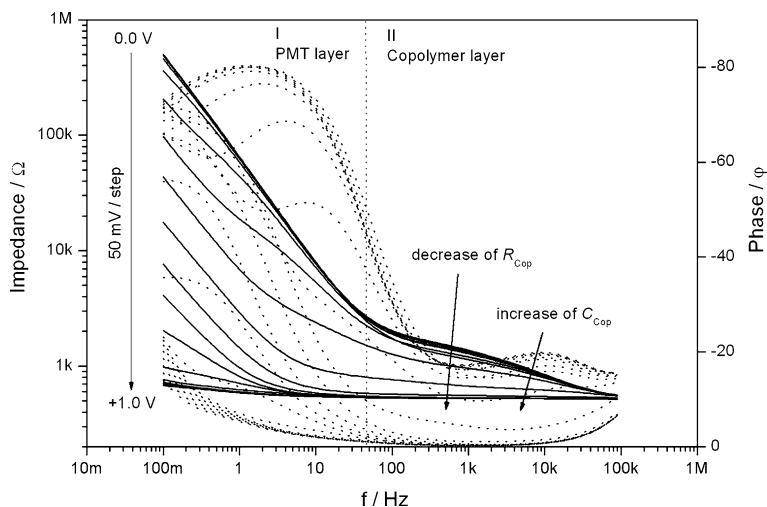


Fig. 9 Bode plots of Cop1/15 film at different applied potentials (*solid lines*), modulus of impedance, and (*dotted lines*) phase shift, recorded in 0.1 M $N(\text{Bu})_4\text{PF}_6/\text{acetonitrile}$ solution



capacitance and corresponding resistance can be attributed to the copolymer layer (see region II). In other words, the charge transfers relating to the redox process of the copolymer backbones was found in the high-frequency range. It was found that the copolymer film Cop1/15 is compact enough to form a space-charge region during reduction process. As a result, a space-charge capacitance was found, if the copolymer film was switched from the doped state to the undoped state.

The impedance data were analyzed by an equivalent circuit in Fig. 10 [21]. In the semiconducting state of the Cop1/15 film, two space-charge capacitances C_{SC} were observed. The space-charge capacitance of the copolymer film at high-frequencies was observed in the potential range from 0.00 V to +0.55 V. The low-frequency capacitance in the potential range from 0.00 V to +0.35 V was attributed to the PMT layer. In this state, the Mott–Schottky equation can be used to analyze the data [20]:

$$C_{SC}^{-2} = \frac{2}{e\epsilon\epsilon_0 N} \left(E - E_{FB} - \frac{kT}{e} \right), \quad (1)$$

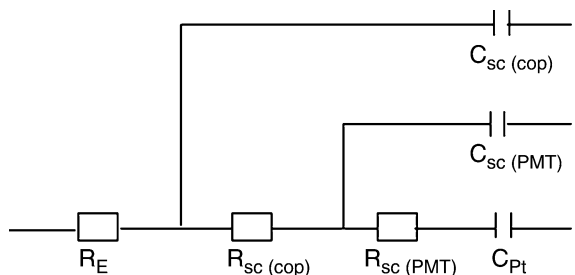


Fig. 10 Equivalent circuits for polymer Cop1/15. $C_{SC(Cop)}$ and $C_{SC(PMT)}$ are the space-charge capacitances of the copolymer and PMT, respectively. $R_{SC(Cop)}$ and $R_{SC(PMT)}$ are the space-charge resistances of the copolymer and PMT layers, respectively. R_E is the electrolyte resistance and C_{Pt} the capacitance of platinum electrode

where ϵ is the dielectric constant of the polymer film, ϵ_0 the permittivity of the free space, e the charge of the electron, N the carrier density, E the applied potential, and E_{FB} the flat-band potential. At room temperature (25 °C), kT/e is approximately 26 mV and can be neglected.

In order to interpret the impedance data, it was assumed that the copolymer film formed electrochemically is considered as bilayer [21]: a thin PMT layer is formed on the electrode surface, due to its lower oxidation potential, and then a copolymer layer of MT and ETA is formed on that polymer-modified electrode. Mott-Schottky plots of the space-charge capacitances C_{SC} are shown in Fig. 11. Two values of flat-band potential E_{FB} were determined by the interception of the straight line with the E axis. One value ($E_{FB} = +0.35$ V) corresponds to that of the pure PMT film and the other value ($E_{FB} = +0.49$ V) is characteristic of the copolymer. The obtained result confirms the formation of a bilayer, consisting of a very thin PMT homopolymer layer and a copolymer (Cop1/15) layer.

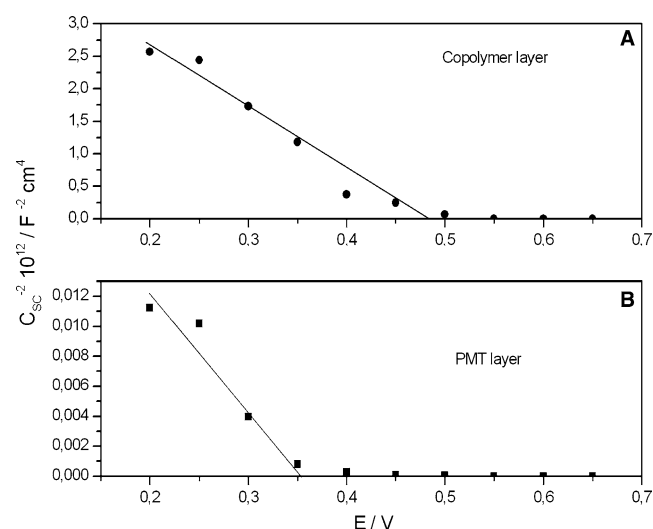


Fig. 11 Mott-Schottky plots of Cop1/15 film for capacitances evaluated at different frequency regions: **a** high-frequency region; **b** low-frequency region

Photocurrent measurement

The results derived from EIS measurements were confirmed by photocurrent measurements. The dependence of the cathodic photocurrent for Cop1/15 and PMT films on the light energy at an applied potential of -0.20 V is shown in Fig. 12. For Cop1/15 two maxima were observed, one maximum at 550 nm corresponding to that of PMT film and another at 470 nm attributed to the semiconducting behavior of the copolymer layer. These photocurrent maxima are characteristic of the $\pi-\pi^*$ transition [20].

The analysis of the photocurrent spectra based on the Gärtner-Butler model [21] is given in Fig. 13. Values of the direct band gap energy E_g^{di} of homopolymer/copolymer films were determined at the interception point of the linear range of the plots with the $h\nu$ axis. The values of E_g^{di} are summarized in Table 2. For Cop1/15, two linear regions were found. The first line intercepting the $h\nu$ axis at 1.99 eV is related to E_g^{di} of the pure PMT

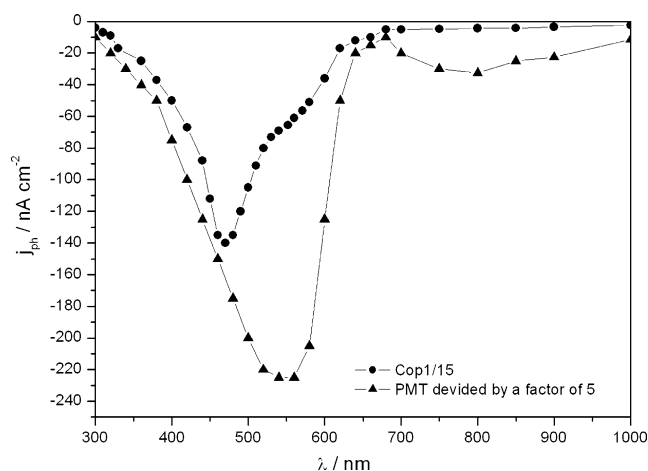


Fig. 12 Cathodic photocurrents of homopolymer/copolymer films at $E = -0.2$ V, recorded in 0.1 M $N(\text{Bu})_4\text{PF}_6/\text{acetonitrile}$ solution

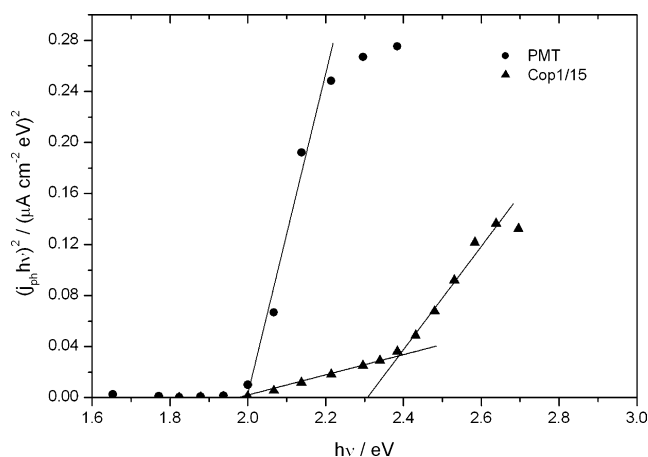


Fig. 13 The $(j_{ph} h\nu)^2$ vs. $h\nu$ plots for determining E_g^{di}

Table 2 Semiconducting parameters of the homopolymer/copolymer films determined by photoelectrochemistry (PEC) and electrochemical impedance spectroscopy (EIS) **a** Values of the thin PMT layer and **b** Values of the copolymer layer

Samples	E_g^{di}/eV	Flat band potential E_{FB}/V	
		PEC	EIS
PMT	1.99	+0.35	+0.35
Cop1/15	1.99 ^a / 2.28 ^b	+0.52	+0.35 ^a / +0.49 ^b
PETA	-	-	-

film. The second line intercepts with the $h\nu$ axis at $E_g^{di} = 2.28$ eV is associated with the direct transitions of the copolymer layer.

The dependence of the photocurrent of the homopolymer/copolymer films on the applied potential is shown in Fig. 14. The onset potentials of the photocurrent spectra corresponding to a flat-band potential E_{FB} were found at +0.35 V for the pure PMT and at +0.55 V for the copolymer. The values E_{FB} are also summarized in Table 2. In the photoelectrochemical behavior of the Cop1/15, the photocurrent signals were generated by both copolymer and PMT layers as polarizing at potentials lower than E_{FB} of PMT film; however, the photocurrent was only generated by copolymer layer if the Cop1/15 was polarized at potentials higher than +0.35 V.

Conclusions

The investigation of the copolymer (MT and ETA) with different methods confirmed that true copolymers with improved mechanical strength and electroactivity were formed. It was shown by ESI mass spectroscopy that statistical combinations of MT and ETA in the co-oligomers were observed in the electrolyte after copolymerization.

One value of the glass transition temperature T_g for Cop1/15 (69.8 °C) and Cop1/30 (76.9 °C) found in DSC curves confirms the formation of a homogeneous copolymer phase. Thermal stability of PETA is less, whereas thermal stability of the copolymers increased with increasing MT content inside the copolymer film. These results were also confirmed by SEM measurement.

Analysis of impedance and electrochemical spectra exhibited that the PETA film possesses almost redox active centers at the surface, but very poor ones inside the polymer chains. The PETA film with an extended π -conjugation was achieved by the copolymerization with 3-methylthiophene.

Impedance and photocurrent measurements showed that the undoped copolymer behaves like a semiconductor with a flat-band potential $E_{FB} = +0.49$ V and a band gap energy $E_g = 2.28$ eV. Also, semiconducting properties of the homopolymer PMT ($E_{FB} = +0.35$ V

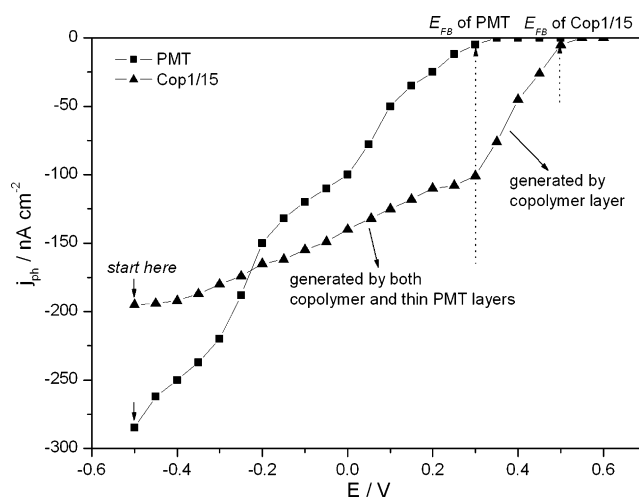


Fig. 14 The j_{ph} vs. E plots of the homopolymer/copolymer films at $\lambda = 500$ nm, recorded in 0.1 M $N(\text{Bu})_4\text{PF}_6/\text{acetonitrile}$ solution

and $E_g = 1.99$ eV) were found. The results illustrated that a bilayer with PMT layer inside and copolymer outside was formed during the electropolymerization process.

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