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Note

Electrochemical synthesis of EDOT–ECZ–EDOT copolymer on carbon fiber micro-electrodes

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Abstract

3,6 bis(3,4-ethylenedioxythiophenyl)-9-Ethylcarbazole (EDOT-ECZ-EDOT or EEE) films are coated electrochemically onto carbon fiber micro-electrodes. Deposition conditions on the electroactivity of the resulting polymers are studied. Structural studies of the polymers have been conducted using different techniques such as cyclic voltammetry, ATR-FTIR, scanning electron microscopy and four-point probe conductivity.

1. Introduction

Conducting and redox active polymers have attracted attention due to their wide application, and their inexpensive and potentially processable nature [1]. Functional conjugated polythiophenes, in which the electronic properties inherent to the p-conjugated systems are associated with new specific properties afforded by covalently attached functional groups, have been the focus of considerable attention during the past decade [2–9]. 3,4-ethylenedioxythiophene (EDOT) is a new thiophene derivative combining high conductivity of its polymer, low band gap, good electrochemical properties and exceptional thermal stability in the oxidized state [10–13].

The processibility of EDOT based materials can be improved by incorporating solubilising segment such as *N*-alkylcarbazole in the PEDOT main chain [14–16, 20] and poly[3,6-bis(2-(3,4-ethylenedioxy)thienyl)*N*-methylcarbazole] was employed as anodically colored material in an electrochromic device.

Previously it has been reported that bis-heterocycle-substituted arylene monomers polymerize easily to form stable electroactive polymers [9–19]. They exhibit very low optical band gap and switch between different colors, which is potentially useful for electrochromic devices.

Further control of the electropolymerization conditions, such as the use of different substrates and the stability of the resulting polymer can contribute to expand the scope of the technological applications of conducting polymers, i.e., reinforcement of carbon fibers (CFs). CFs were electrochemically deposited by electroactive monomers, such as pyrrole, thiophene, carbazole, 3-methylthiophene and aniline [21–26].

In this study 3,6 bis(3,4-ethylenedioxythiophenyl)-9-ethylcarbazole was synthesized by Stille coupling instead of Grignard coupling, as reported before for *N*-methyl derivative [16], and the determination of the optimum conditions for preparation of an electroactive polymer on CF was studied.

2. Experimental

2.1. *Materials*

All chemicals were used as received from Aldrich Chemical without further purification. High strength (HS) CFs C 320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320 000 single filaments in a roving were used as working electrodes. All the electrodes were prepared by using CF (diameter = 7 μm) attached to a copper wire with Teflon tape. The electrode area was kept constant ($\sim 6.0 \times 10^{-4}$ cm^2) by adjusting the dipping length and covering the rest of the fibers with the Teflon tape.

2.2. *Fiber surface morphology*

Surface morphology of all electrografted fibers were analyzed by scanning electron microscopy (SEM) using a Hitachi S-2700 SEM (Nissei Sangyo GmbH, Rathingen, Germany), which was connected to an energy dispersive X-ray microanalyzer (EDX) (Kevex type

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delta V, Foster City, CA, USA). The excitation energy was 10 keV at a beam current of 0.5 nA. with ×6000 multiplication factor.

2.3. *ATR–FTIR reflectance measurements*

Thin polymer films which were electrografted onto the CF surface were analyzed by FTIR reflectance Spectrometer (Perkin-Elmer with an ATR attachment of spectrum one Universal ATR with diamond and ZnSe).

2.4. *Polymerization*

Polymerization reactions were performed electrochemically at constant potential in propylene carbonate (PC) solution containing 0.1 M $LiClO_4$ and monomer. Cyclic voltammetry (CV), of the polymers was performed with a Wenking POS 73 potentiostat in a three-electrode cell employing CF (area $= 6.0 \times 10^{-4}$ cm^2) as the working electrode, platinum as the counter electrode, and a silver wire as a quasireference electrode. It was calibrated using the ferrocene (Fc/Fc^+) redox couple which has a formal potential $E_{1/2} = +0.320$ V vs silver wire. Electrodeposition was carried the out from a 10^{-2} M solution of monomer in 0.1 M electrolyte at a scan rate of 20 mV s^{-1} for different cycles.

3. Results and discussion

The cyclic voltammograms obtained during polymer film growth on both Pt and CF electrodes are presented in Figure 1a and b, respectively. The oxidation of monomer starts at approximately 0.54 V on Pt, and 0.22 V on CF, and gives a peak at 0.62 V on Pt and 0.43 V on CF electrodes, respectively. Upon repeated scans new redox processes appear at lower potentials, indicating the formation of an electroactive polymer film. Reversibility of film seems better in the case of the CF electrode. Polymer films were obtained at different scan numbers, and their SEM photographs were taken (Figure 2). As the scan number increases a shoulder forms at around 0.1 V, which may be due to more delocalized electronic structures, thus decreasing the onset of anodic current which became more significant. As may be seen in the SEM pictures increasing the scan numbers, increase the film thickness (Figure 2). From SEMs cross section of the electrodes (Figure 2e) the thickness was calculated, as the thickness of unmodified CF is known. Using the data obtained from these measurements a graph of scan number against thickness was plotted (Figure 3).

FTIR–ATR measurements of freestanding PEEE film were taken and the results are summarized in Table 1, which agrees with characteristics of both EDOT and ECZ as suggested in the literature [27–29].

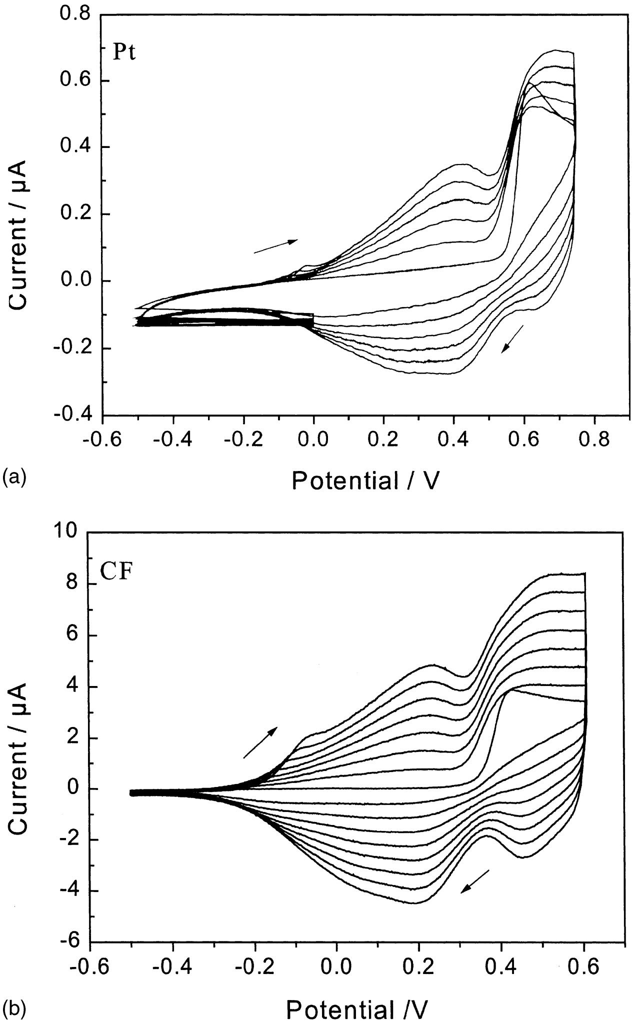

Fig. 1. Cyclic voltammograms for the oxidation of EEE on Pt (a) and CF (b) in 0.1 M $LiClO_4$ containing PC at 20 mV s^{-1}.

3.1. *Redox behaviour and stability of PEEE films*

The redox behaviour of polymer obtained at different scan numbers was tested in monomer free supporting electrolyte by CV (Figure 4). The scan rate dependence of the peak currents was found to scale linearly, indicative of an electrode supported electroactive film (Figure 4). Similar slopes for anodic and cathodic peak currents also support reversible redox behaviour of the film, and the performance is better than previously reported on Pt electrodes [16]. Depending on the scan number during synthesis, the peak potentials and formal potentials of the polymer film shift anodically as the thickness increases ($E_{1/2}$, $V = 480$ for 3rd cycle and $E_{1/2}$, $V = 490$ for 10th cycle). This may be due to the difficulty of electron transfer in samples with increased thickness.

The *in situ* spectroelectrochemical spectrum of PEEE shows the evolution of mid-IR absorptions as the polymer becomes conducting and shows fast switching times (in seconds) for the large optical changes being attained (Figure 5). The optical band gap of the film obtained was 2.48 eV, which is very close to that of *N*-methyl derivative reported previously [20]. In the fully

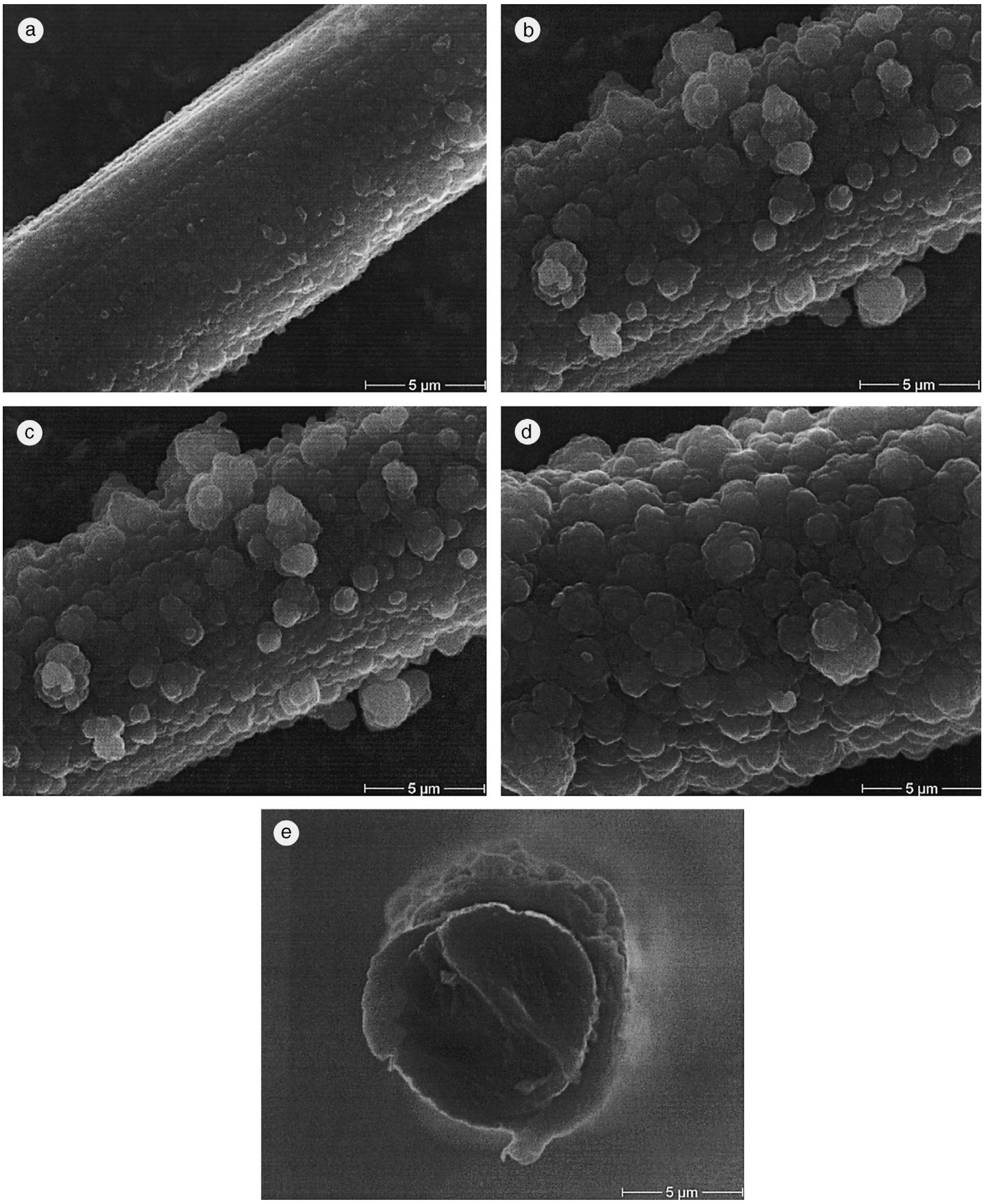

Fig. 2. SEM pictures of PEEE films on CF obtained at different scan numbers: 3 (a), 10 (b), 15 (c), 20 (d), and cross section (e).

reduced form (at −1.0 V) the polymer is yellow but the color gradually changes to green with mildly oxidizing potential (at 0.1 V) and at higher potential it turns to deep blue. This type of multicolor behaviour is not common but is important for the preparation of electrochromic materials.

The stability of the polymer films was tested by CV. After the preparation of polymeric film on CF electrodes at different scan numbers (5th cycle and 10th cycle), they were exposed to different potentials in the range −1.0 to +1.2 V for 5 min and cyclic voltammograms of films in monomer free electrolyte at different scan rates were measured. The percentage decrease in electroactivity at each applied potential and scan rates were calculated as follows:

$$\text{Percentage decrease in electroactivity (PDEA)} \\ = [(Q_{\text{before}} - Q_{\text{after}})/Q_{\text{before}}] \times 100$$

where Q_{before} is the redox capacity in coulombs for a freshly prepared electrode in monomer free electrolyte and Q_{after} is the redox capacity after application of applied potentials. Results are shown in Figures 6 and 7. Both electrodes prepared potentiodynamically by applying 5 cycles and 10 cycles are stable up to 1.2 V which is a sufficiently high oxidation potential (oxidation potential of the polymer is 485 mV). At 1.2 V only a 1% decrease was observed. The redox behaviour of thicker films prepared at higher scan number (20 cycles) by CV shows quasi-reversible behaviour.

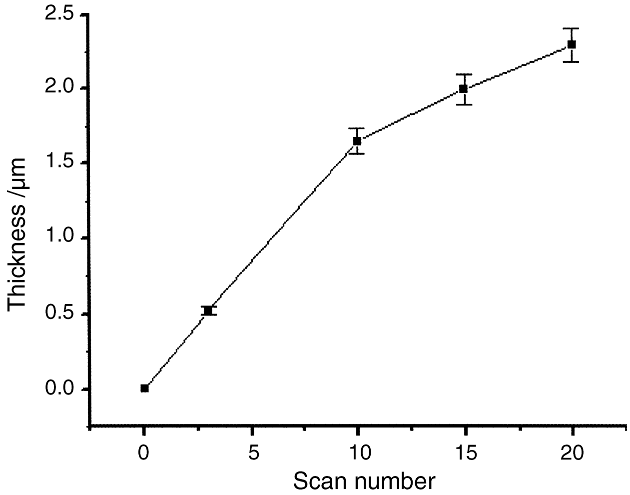

Fig. 3. Variation of thickness of polymer film with scan number.

Table 1. Proposed assignment for the main vibration for PEEE film

Wavenumber /cm^{-1}	Assignments
2601	ν(C—C)
1619, 1579, 1472, 1441	ν(C—C)$_{ring}$
1336	ν(C—CH$_3$) of ECZ
1299, 1258, 1226, 1157	ν(C=C) ν(C—C) of thiophene ring and ν(—COROC—)
1046, 622	Doping induced band
931, 908, 847, 808, 750, 710	ν(C—S) and δ(C—S) and δ(C—H)

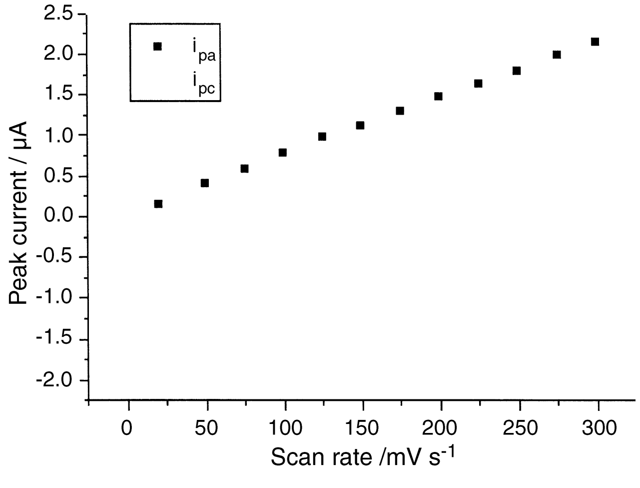

Fig. 4. Scan rate dependence of PEEE film in monomer free supporting electrolyte and variation of peak current with scan number.

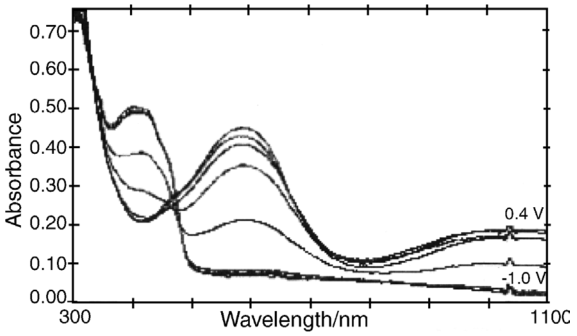

Fig. 5. In situ spectroelectrochemistry of PEEE film obtained at different applied potential in the range of −1.0 to 0.4 V.

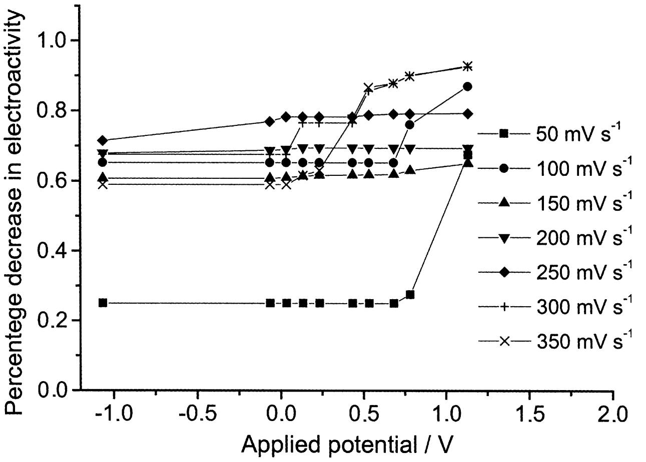

Fig. 6. Variation of percentage decrease in electroactivity with different applied potential at different scan rates for PEEE electrode (at 5th cycle).

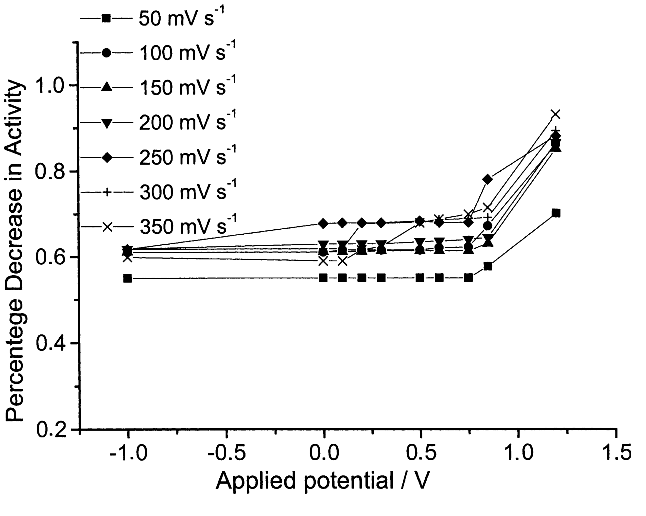

Fig. 7. Variation of percentage decrease in electroactivity with different applied potential at different scan rates for PEEE (at 10th cycle).

4. Conclusion

PEEE films were prepared on flexible CF electrodes and the electrodeposition conditions of the monomer were studied. The polymeric films give rise to an array of different colors, dependent on deposition conditions and film thickness. Simple alternative methods were suggested for the determination of polymeric film thickness on CF electrodes. The films were found to be very stable even at high potential.

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