

# Synthesis and Electrochemical Polymerization of *N*-Ethylcarbazole-bis-3,4-ethylenedioxythiophene-*N*-ethylcarbazole Comonomer

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**ABSTRACT:** A new comonomer ECz-BEDOT-ECz (EBEE) [ECz: *N*-ethylcarbazole-BEDOT:2,2'-bis(3,4-ethylenedioxy)thiophene] has been synthesized, characterized, and electropolymerized on Pt and carbon fiber microelectrodes (CFME). The ECz side group of the comonomer plays an important role in determining its physical properties PEBEE and it resembles the behavior of corresponding homopolymer (PECz). PBEDOT was increased by the incorporation of ECz

monomer into structure. The environmental stability of PBE-DOT was increased by incorporating the ECz unit into the structure. The new comonomer seems prefer to be electrodeposited onto CFME as opposed to Pt. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 795–801, 2007

**Key words:** electropolymerization; ECz-BEDOT-ECz comonomer; carbon fiber and Pt electrodes

## INTRODUCTION

*N*-alkyl substituted 3,6-ethylenedioxythienyl carbazoles (EDOT-MeCz-EDOT) have been synthesized and electropolymerized.<sup>1</sup> An unsubstituted thiophene analogue has also been recently prepared and polymerized.<sup>2</sup> These materials display two distinct reversible oxidation processes that allow for the existence of three redox and corresponding color states useful for electrochromic applications. Moreover, the importance given to these polymers, by well known high technological value of Cz, does not need to be highlighted.

The ability to form coherent polymer films depends greatly on the electrode material and the nature of its substituents such as *N*-ethyl and *N*-phenyl that do not allow the film formation on the Pt anode substrate in acetonitrile, though film formation is possible in HClO<sub>4</sub> on Au electrode.<sup>3–7</sup>

Carbon fiber microelectrodes (CFMEs) are stable and commercially available. Their disposable nature and low cost open a wide range of potential applications and biosensor applications.<sup>8</sup> CFME have been used in the detection of biologically important analytes such as dopamine.<sup>9</sup>

In our previous study, we had investigated the electrochemical behavior of EDOT-ECz-EDOT<sup>10</sup> and its copolymer (and composite) with BEDOT. In this work, ECz-BEDOT-ECz was synthesized for the first time

and electropolymerized to investigate the effect of the ECz side groups on the properties of the resulting polymer. To obtain an electroactive film on the platinum electrode, the effect of switching potentials on polymer growth was investigated. However, film formation was not observed on Pt, as the product obtained was soluble. In contrast, electropolymerization of ECz-BEDOT-ECz comonomer on CFME was achieved.

## EXPERIMENTAL

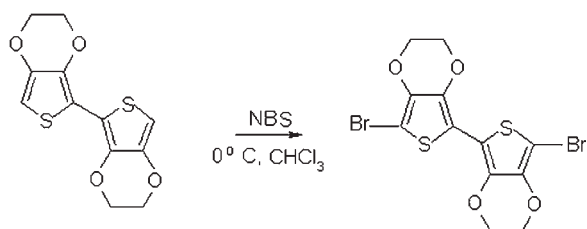
### Materials

All chemicals were used as received from Aldrich Chemical without further purification. High strength carbon fibers C 320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320,000 single filaments in a roving were used as working electrodes. All of the CFME electrodes (in general ~ 100 single fibers were used except for a few cases when 30 single fibers were used) were prepared by using carbon fibers (diameter ~ 7 μm) and attached to a copper wire with a Teflon tape. The Polymerization reaction was carried out electrochemically in propylene carbonate (PC) solution containing 0.1M LiClO<sub>4</sub> and monomers.

### Instrumentation

The cyclic voltammograms (CV) of polymers were obtained with a Parstat 2263 potentiostat/galvanostat in a three-electrode setup employing CFME or Platinum (button electrode) as the working electrode

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**Scheme 1** Bromination of BEDOT.

(anode). The reference electrode was Ag-AgCl (electrode was kept in 3M NaCl when it is not in use).

Electrocoated fibers were analyzed by scanning electron microscopy (SEM) using a JEOL (Tokyo Japan) JSM S410 scanning electron microscope that was connected to a EDS-X-ray energy dispersion spectroscopy micro analyzer, Noran Voyager II Quantitative micro-analysis with a Freedom detector (Noran Instruments, Japan). The excitation energy was 5 keV at a beam current of 60  $\mu$ A.

The Polymer electrografted on the carbon fiber surface was analyzed by FTIR-reflectance spectrometer (Perkin-Elmer Spectrum One B with a Universal ATR attachment with diamond and ZnSe). The UV spectrum of monomer solution was acquired by a UV-vis spectrophotometer (160A Shimadzu).

## Synthesis

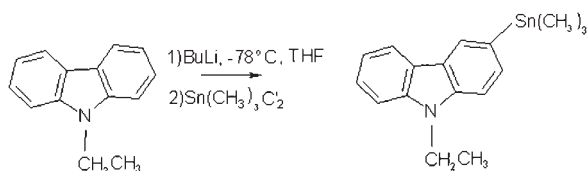
Bis-3,4-ethylenedioxythiophene (BEDOT) was prepared via Ullmann coupling utilizing lithiated EDOT and copper(II) chloride as described earlier.<sup>11</sup>  $^1\text{H}$  NMR peaks were obtained as:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 4.3 ppm (4H, s), 6.2 ppm (2H, 2).

Table I listed some characteristic peaks of BEDOT, a peak at 1565  $\text{cm}^{-1}$  is due to  $\nu(\text{C}-\text{C})_{\text{ring}}$ , a peak at 1170  $\text{cm}^{-1}$  evident for etheric bands, the peaks at 948(s) and 896(s)  $\text{cm}^{-1}$  are attributed to thiophene  $\nu(\text{C}-\text{S})$  and  $\delta(\text{C}-\text{S})$  vibrations.

## Bromination of BEDOT (Scheme 1)

*N*-Bromosuccinimide (0.8 g, 4.5 mmol) in  $\text{CHCl}_3$  (50 mL) was added to a stirred solution of BEDOT (0.6 g, 2.1 mmol) in  $\text{CHCl}_3$  (40 mL). The reaction mixture was stirred for 3 h at 0°C under nitrogen atmosphere.



**Scheme 2** Synthesis of 3-trimethyltin-9-ethylcarbazole.

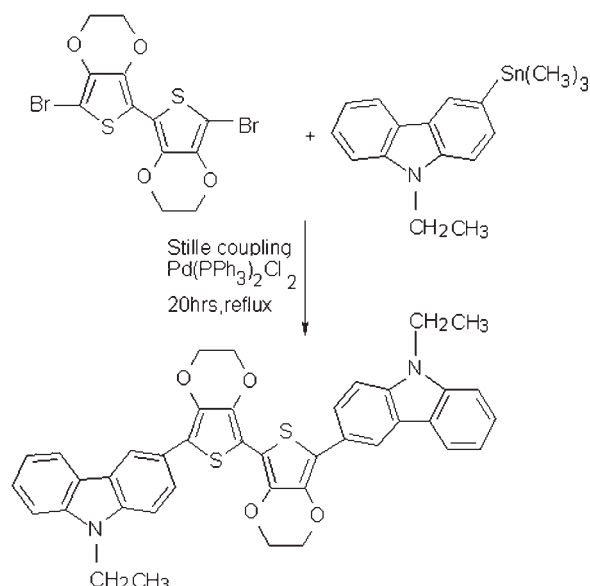
**TABLE I**  
Proposed Assignments for the Main Vibrations of BEDOT Comonomer

Wavenumber ( $\text{cm}^{-1}$ )	Assignments
1565(s), 1451(s)	$\nu(\text{C}-\text{C})_{\text{ring}}$
1170(s), 1142(s)	$\nu(\text{C}=\text{C})$ of thiophene ring and $\nu(-\text{C}-\text{O}-\text{C}-)$
948(s), 896(s), 774(s), 699(s),	$\nu(\text{C}-\text{S})$ and $\delta(\text{C}-\text{S})$ and $\delta(\text{C}-\text{H})$

Then it was poured into water and extracted with  $\text{CHCl}_3$ . Organic extracts were dried with  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated and dried under vacuum. The overall yield was 70% and its  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  contains a peak at  $\delta$  = 4.3 ppm that corresponds to ethylenedioxythiophene ring. The disappearance of the peak at  $\delta$  = 6.2 ppm for the protons in thiophene ring indicates dibromination.

## Synthesis of 3-trimethyltin-9-ethylcarbazole (Scheme 2)

ECz (1.0 g, 5.12 mmol) was added to a 30 mL THF under nitrogen purge. The solution was cooled down to  $-78^\circ\text{C}$  with the help of liquid  $\text{N}_2$  bath. *N*-BuLi (3 mL, 5.12 mmol 2.5M in hexane) was added to this solution. The resulting solution was stirred for 1 h, then trimethyltin chloride (1.2 g, 5.12 mmol) was added. The reaction mixture was stirred for another hour at  $-40^\circ\text{C}$ , and then at room temperature for a further 24 h. After the reaction was completed, the solution was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . Organic extracts was dried with  $\text{Na}_2\text{SO}_4$ . The oily golden brown product was left in vacuum overnight.



**Scheme 3** Stille coupling.

**TABLE II**  
Proposed Assignments for the Main Vibrations of ECz-BEDOT-ECz Comonomer

Wavenumber (cm <sup>-1</sup> )	Assignments
2980(v), 3050(s)	$\delta(\text{C-H})$ (aromatic C-H)
1616(s), 1500(s), 1466(s)	$\nu(\text{C-C})_{\text{ring}}$
1316(s)	$\nu(\text{C-CH}_3)$ of ECz
1283(w), 1250(s), 1166(s)	$\nu(\text{C=C})$ , $\nu(\text{C-C})$ of thiophene ring, and $\nu(-\text{O-C-O-})$
931(s), 908(s), 847(s), 808(s), 750(s), 710(s)	$\nu(\text{C-S})$ , $\delta(\text{C-S})$ , and $\delta(\text{C-H})$

s, strong; w, weak; v, variable.

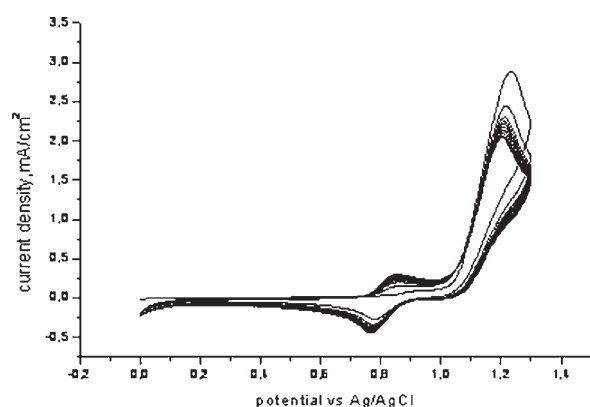
<sup>1</sup>H NMR of product (in CDCl<sub>3</sub>)  $\delta = 8.09$  ppm (2H, d), 7.4–7.3 ppm (5H, m), 4.2 ppm (2H, t), 1.2 ppm (3H, d), 0.35 ppm (9H, s).

### Synthesis of ECz-BEDOT-ECz

Bis(triphenylphosphine) palladium(II) chloride (0.02 g, 0.5 mmol) was added into a solution of dibromoBEDOT (0.5 g, 1.14 mmol) and 3-trimethyltin-9-ethylcarbazole (0.4 g, 1.11 mmol) in 100 mL THF (refluxed under N<sub>2</sub> atmosphere for 24 h). The reaction mixture was poured into water. It was extracted with CHCl<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub> and then kept in vacuum. The crude product was purified by flash chromatography on a SiO<sub>2</sub> column eluted with petroleum ether–diethyl ether (4/3, v/v). The melting point of ECz-BEDOT-ECz is around 65.5–66.0°C (Scheme 3).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 8.2$  ppm (4H, d), 7.4–7.3 ppm (14H, m), 4.4 ppm (8H, t), 4.2 (4H), 1.25 ppm (6H, d).

Table II obtained from FTIR-ATR spectrum of EBEE indicates the characteristic ECz and EDOT peaks evident for obtaining EBEE comonomer. The peak at 750 cm<sup>-1</sup> is attributed to Cz monomer aromatic C–H out plane vibration, and the peaks at 1283 and 1250 cm<sup>-1</sup> are evident for  $\nu(\text{C=C})$ ,  $\nu(\text{C-C})$  of thiophene ring.



**Figure 1** Potentiodynamic growth of ECz-BEDOT-ECz ( $4 \times 10^{-3}$  M) on Pt electrode in PC containing 0.1 M LiClO<sub>4</sub> (scan rate: 100 mV/s).

**TABLE III**  
Effect of Switching Potential on Redox Parameters of Electrodeposition of EBEE on Pt Electrode

$E_s$ (V)	$E_{\text{onset}}$ (V)	Q (mC)	$E_a$ (V)	$E_c$ (V)	$\Delta E$ (V)	$I_a/I_c$
1.20	0.776	1.163	0.898	0.776	0.122	0.778
1.22	0.756	1.424	0.853	0.775	0.078	0.669
1.24	0.754	1.601	0.846	0.767	0.079	0.682
1.26	0.761	1.557	0.843	0.765	0.078	0.659
1.28	0.753	1.956	0.851	0.768	0.083	0.658
1.30	0.759	1.955	0.847	0.769	0.078	0.676

$E_s$ , switching potential.

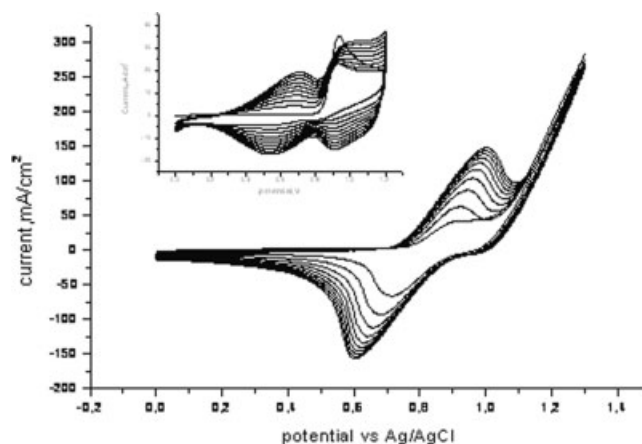
## RESULTS AND DISCUSSION

### Polymer synthesis and characterization

The electropolymerization of ECz-BEDOT-ECz (EBEE) comonomer on CFME and Pt was studied. Electropolymerization of ECz on CFME electrode was also carried out to compare with the results of the comonomer.

A CV was obtained for electropolymerization of ECz-BEDOT-ECz on Pt to see the differences in film growth at different switching potential (Fig. 1). The redox parameters determined by CV results were summarized in Table III. The results show that there is no significant difference between the anodic and cathodic scans with increasing switching potential.

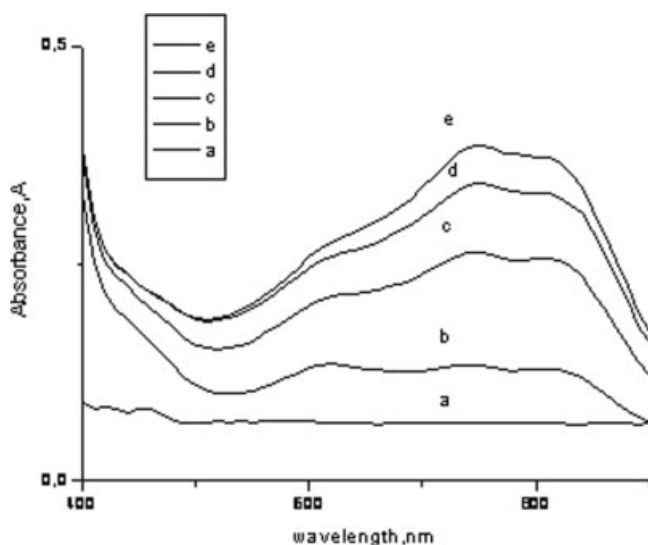
Electropolymerization of the EBEE comonomer on CFME was achieved by applying potential cycling between 0 and 1.3 V at a scan rate of 100 mV/s (Fig. 2). The first redox process (0.89 V in the positive scan and 0.70 V in the negative scan) corresponds to electron transfer from/to the electrodeposited PolyEBEE film. To compensate for the charge of the film, anion transport from/to electrolyte solution, anion doping, and dedoping should occur. The second redox process has large currents due to the superposition of two



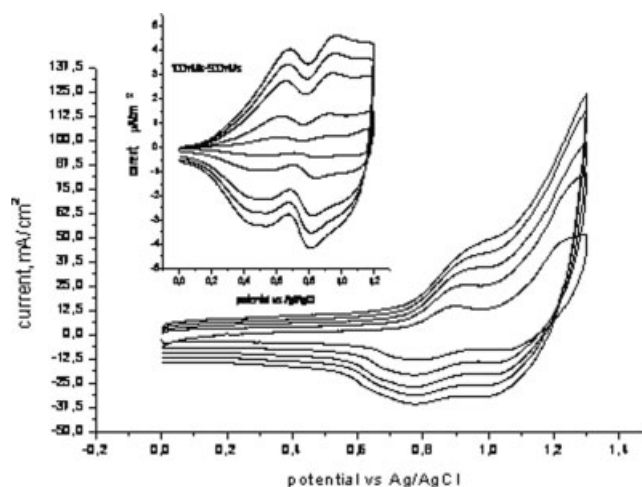
**Figure 2** Potentiodynamic growth of ECz-BEDOT-ECz on CFME electrode in LiClO<sub>4</sub>/PC. Inset: potentiodynamic growth of EEE on CFME electrode in LiClO<sub>4</sub>/PC.

distinct processes; one is the electron transfer from EBEE comonomer to the electrode corresponding to oxidation of comonomer to produce the precursor for PEBEE film, the other is the electron transfer from PEBEE film corresponding to oxidation of PEBEE film.

Although current intensities increase as the scan number increases, deposition process or insoluble film formation could not be observed when Pt electrode was used as the working electrode (Fig. 1). In the mean time, the color of the solution turned blue because of the so-called oligomer approach that was accepted recently.<sup>12,13</sup> In this approach, it is suggested that the formation of the dimer and subsequent dimerization step leads to the formation of soluble oligomers. After that, deposition and growth processes triggered by nucleation reaction occurred. In addition, recent studies showed that the rate constant of dimerization for forming chain-like conjugated oligomers and their coupling steps with the original monomers decrease with increasing chain length.<sup>12–22</sup> In our case, after dimerization and/or tetramer formation, further coupling reactions become very slow because of the decrease in the rate constant. The diffusion of oligomers into the bulk solution from the vicinity of the electrode surface does not allow them to couple because the bulk solution is less concentrated than the electrode surface during electropolymerization process on Pt, since bonding can start on carbon fiber and lead to further chain growth on the carbon fiber by the increase of oligomer concentrations on the surface. Formation of only soluble oligomers in solution was also supported by the color change of solution that turned from colorless to blue as the reaction proceeds (Fig. 3).



**Figure 3** UV-visible spectrum of EBEE comonomer solution during electropolymerization on Pt electrode: (a) 0 s; (b) 30 s; (c) 90 s; (d) 135 s; (e) 190 s.



**Figure 4** Scan rate dependence of P(ECz-BEDOT-ECz) on CFME in 0.1M LiClO<sub>4</sub>/PC. Inset: scan rate dependence of PEE on CFME electrode in LiClO<sub>4</sub>/PC.

The increase in current obtained from each scan during polymer growth was compared for Pt and CFME. It can be easily seen that they are higher in the case of CFME (Figs. 1 and 2). This result suggests the formation of the conducting film on CFME surface by electropolymerization.

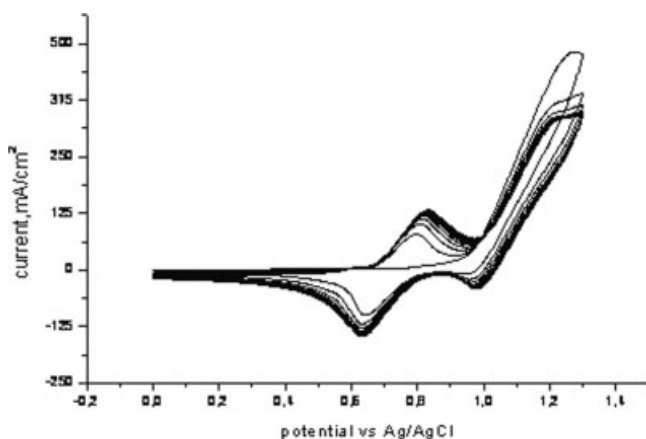
To study the redox properties, the electrochemically deposited PEBEE film was investigated after the film deposited CFME was washed with PC and was placed into a monomer-free electrolyte solution. Figure 4 shows the CV of PEBEE at different scan rates. As illustrated in Figure 4, the current is linearly proportional to the scan rate, indicating that the electroactive polymer film was electrodeposited on CFME, i.e., the resulting polymer displays two oxidation processes, at 0.88 and 1.22 V (Fig. 4).

Table IV listed the onset potentials of the monomers and the half wave potentials for redox processes of the corresponding polymers. The redox potential of PEBEE redox potential is 0.40 V lower than that of PECz. In our previous study, the  $E_{1/2}$  and  $E_{onset}$  values of another comonomer (EEE) of EDOT end-capped with ECz<sup>10</sup> are smaller than those of ECz and EBEE. PEEE has longer conjugated length and lower band gap.

**TABLE IV**  
Redox Parameters of Monomers and Polymers

Monomer	$E_{onset,m}$	$E_{1/2,p}^a$
ECz	0.64	1.22
EBEE	0.70	0.82
EEE <sup>10</sup> (EDOT-ECz-EDOT)	0.13	0.48
BEDOT	-0.30	0.15

<sup>a</sup>  $E_{1/2}$  was calculated at 100 mV/s scan rate in LiClO<sub>4</sub> containing PC.

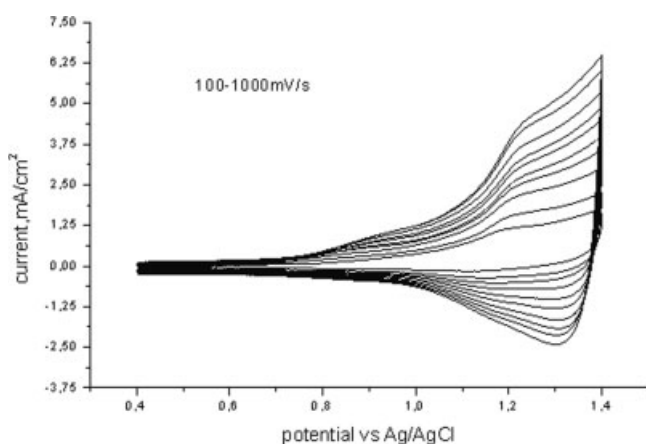


**Figure 5** Potentiodynamic growth of ECz ( $2 \times 10^{-3}M$ ) on CFME electrodes in  $0.1M LiClO_4/PC$  (scan rate:  $100 mV/s$ ).

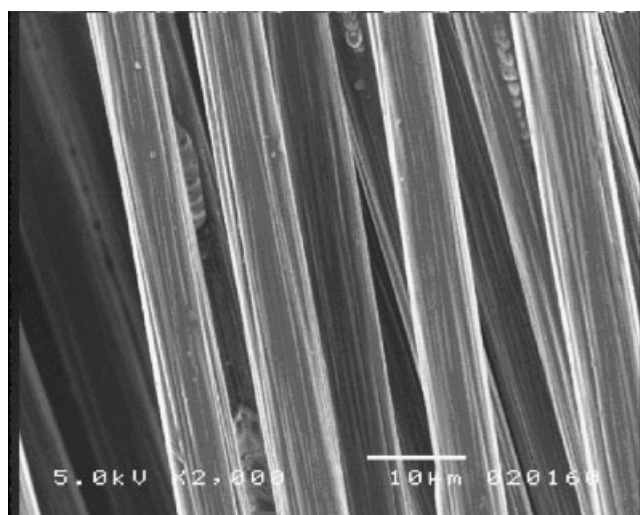
The achievement of anodic oxidation product as coherent films depends on the nature of electrode and medium,<sup>3-6</sup> i.e., in acetonitrile, only soluble oligomers obtained when using Pt electrodes, while insoluble deposition obtained on Au and glassy carbon electrodes. In our case since the comonomer EBEE contains ECz end group, it possesses the properties of ECz. During the course of electropolymerizing soluble oligomers with platinum, *in situ* spectroelectrochemical investigation supported the soluble oligomer formation, as absorbances at 760 and 820 nm increases with the electropolymerization time (Fig. 3).

In our and other previous studies, comonomer EEE gave insoluble polymers on both Pt and CFME electrodes under similar conditions.<sup>8,10,23-25</sup>

To gain a better understanding on the electropolymerization behavior of EBEE, ECz was also studied under the same conditions with both Pt and CFME electrodes comparatively. But in the case of Pt electrodes, no electrodeposition was obtained and only a soluble green oligomer was formed in solution as suggested before.<sup>3-6,25-30</sup>

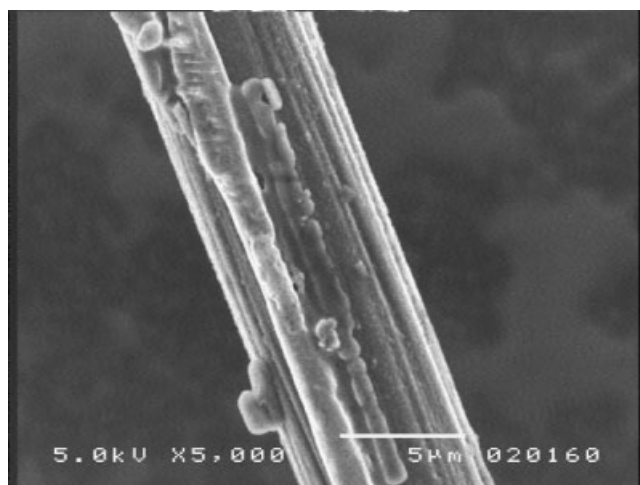


**Figure 6** Scan rate dependence of PECz-coated CFME in  $0.1M LiClO_4/PC$ .

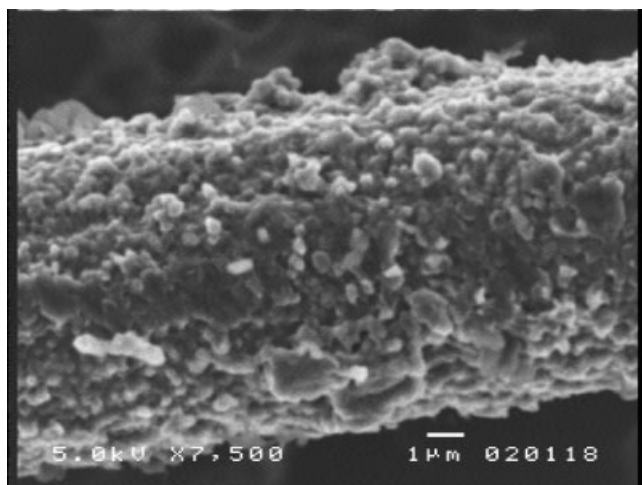


**Figure 7** PEBEE obtained with  $100 mV/s$ , three cycle in  $LiClO_4/PC$  on CFME.

On the other hand, under the same conditions, electrodeposition of ECz was successfully achieved on CFME electrode in nonaqueous solvent for the first time. As can be seen from the CV obtained during polymerization (Fig. 5), the current intensity increased with subsequent scans. The CV of PECz (Fig. 6) unambiguously indicate that the oxidative doping of this polymer is a two-step phenomena since two redox species are seen ( $0.93$  and  $1.23 V$ ). These two redox processes have been assigned to the formation of radical cation and dication states within the carbazole unit.<sup>29</sup> Similar results were also observed for poly(3-octyl thiophene).<sup>30</sup> In addition, the CV of PECz-coated CFME electrodes in monomer-free electrolyte shows two oxidation steps located at around  $0.93$  and  $1.23 V$  respectively, and they slightly shifted linearly with subsequent scans (Fig. 6).



**Figure 8** PEBEE obtained with  $100 mV/s$  40 cycle in  $LiClO_4/PC$  on CFME.



**Figure 9** SEM of PEBEE deposited on CFME in  $\text{LiClO}_4/\text{PC}$  with 20 mV/s and 50cycle.

The separation between anodic and cathodic peaks is associated with ion transport resistance involved in these redox reactions. Thus, the difference between the anodic and cathodic peak potentials ( $\Delta E$ ) can serve as an indication for the resistance of ion migration in the electrode.<sup>31–34</sup> CV of EBEE and ECz indicate that the resistance of ion migration of EBEE is higher than that of ECz and also EBEE electrodeposition is faster than ECz's when compared with the current values of monomers (Figs. 2 and 5).

### Morphology

The morphology of the PEBEE films electrodeposited onto CFME potentiodynamically at different scan rates from the monomer solution (4.10–3M EBEE in  $\text{LiClO}_4/\text{PC}$ ) was characterized by SEM. As shown in Figures 7 and 8, the PEBEE polymers obtained at 100 mV/s and different cycle numbers are heterogeneous coatings. However, regular polymer growth was achieved when a slow scan rate (20 mV/s) was employed with 50 cycles (Fig. 9). A globular structure resulting from a three-dimensional nucleation growth mechanism was observed only in this case. The small clusters of globules were observed in the SEM spectrum (Fig. 9), indicating that a more uniform PEBEE film was formed at the slow scan rate (20 mV/s) than those polymer films obtained at the higher scan rate (100 mV/s).

### CONCLUSIONS

The ECz-BEDOT-ECz (EBEE) comonomer was synthesized for the first time and its electropolymerization on Pt and CFME was studied. PolyEBEE (PEBEE) film can readily form on CFME surface and its CV of electrogrowth exhibits two oxidative processes at 0.88 and 1.22 V. However, PEBEE film does not form on Pt

under the same conditions, indicating that the electrode material plays an important role in electrocoating. Because of the nature of CFME, the EBEE oligomers are easily adsorbed or bonded onto the surface of micro-carbon fibers that promotes the film formation of PEBEE. The thickness and the homogeneity of the deposited PEBEE film depend on the scan rate. Similarly, electropolymerization of ECz on CFME under the same conditions was also achieved for the first time. The CV of PECz-coated CFME shows two-step oxidation at 0.93 and 1.23 V. Comparison with our previous studies reveals that the chemical composition of monomers plays an important role in determining the properties of the resulting polymers. The present work has explicitly elucidated that small dimension of carbon fiber leads to a successful electrodeposition that facilitates the favorable properties through the selection of monomer, electrode, and scan rate.

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