

Electrochemical Copolymerization of Carbazole and 3-Methylthiophene

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ABSTRACT: The copolymerization of carbazole (CZ) and 3-methylthiophene (3MeT) was successfully performed electrochemically in freshly distilled boron trifluoride diethyl etherate by direct anodic oxidation of the monomer mixtures, although the oxidation potentials of CZ and 3MeT were quite different. The electrochemical properties of the copolymers were studied with cyclic voltammetry. The influence of the applied polymerization potential on the synthesis of the copolymers was investigated. The higher potential favored the incorporation of 3MeT units into the copolymers. The insertion of 3MeT units into poly-

carbazole (PCZ) was helpful in improving the conductivity of PCZ. The novel copolymers had the advantages of both PCZ and poly(3-methylthiophene), that is, good redox activity, good thermal stability, and high conductivity. The structure and morphology of the copolymers were investigated with ultraviolet–visible, infrared spectroscopy, thermal analysis, and scanning electron microscopy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1877–1885, 2006

Key words: conducting polymers; copolymerization; electrochemistry

INTRODUCTION

Inherently conducting polymers have been investigated since the late 1970s.^{1–3} They have been used as materials for light-emitting devices,^{4–11} color displays, thin-film transistors,^{12–14} and solar cells.^{10,15} Among them, polypyrrole,¹⁶ polythiophene, and their derivatives^{17–19} have received considerable attention. Polycarbazole (PCZ) and its derivatives, having a structure of a pyrrole ring with two fused benzene rings beside it, are well known to exhibit good electroactive and photoactive properties because of the high hole-transporting mobility of the charge carriers.²⁰ Moreover, PCZs, with the advantages of good environmental stability and photoconductivity and electrochromic properties, have attracted great attention because of their wide fundamental interest and potential industrial applications in electroluminescent applica-

tions,^{21–23} light-emitting diodes,^{4,24} electrochromic displays,²⁵ organic transistors,²⁶ rechargeable batteries,²⁷ and so forth. However, the relatively low electrical conductivity ($>10^{-9}$ S/cm in the dedoped state and $>10^{-3}$ S/cm in the doped state²⁸) may inhibit its applications. In addition, it is hard to obtain freestanding films of PCZ. On the other hand, poly(3-methylthiophene) (P3MeT), an important derivative of polythiophene, has also been the subject of intense research because of its high conductivity (close to 750 S/cm²⁹), high tensile strength, and good flexibility.³⁰ These properties make P3MeT applicable to microelectronics, optoelectronics, and sensors. Recently, research has been focused on copolymerization to prepare conducting polymers with better properties and to overcome the limitation of the rarity of new monomers. So far, 3-methylthiophene (3MeT)-based copolymers have been prepared successfully by the direct electrochemical oxidation of mixtures of 3MeT with other corresponding monomers.^{31–37} By means of electrochemical copolymerization, as mentioned previously, some new conducting copolymers have been prepared with obvious advantages, such as the variation of the conductivity, the enhancement of the electrochemical activity, and thermal stability.

It is well known that freestanding films of P3MeT with good properties can be produced by the direct anodic oxidation of 3MeT monomer in boron trifluoride diethyl etherate (BFEE).³⁸ The interactions

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between the middle strong Lewis acid, BFEE, and the aromatic monomers lower their oxidation potentials, and the catalytic effect of BFEE facilitates the formation of high-quality, freestanding P3MeT films. Under these circumstances, BFEE serves not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte is needed. However, PCZ films with relatively poor conductivity prepared from BFEE are brittle, in sharp contrast to P3MeT films. According to the strategy of electrochemical copolymerization mentioned previously, copolymers of carbazole (CZ) and 3MeT would extend the applications of both PCZ and P3MeT. According to the traditional view of electrocopolymerization, the success of copolymerization is mainly due to the closeness of the oxidation potentials of the two monomers. Unfortunately, the oxidation potentials of 3MeT and CZ are quite different, and this has made it a challenge to achieve the electrochemical copolymerization of 3MeT and CZ. To the best of our knowledge, the electrochemical copolymerization of CZ with 3MeT in BFEE has not been reported so far. On the basis of these considerations, it would be interesting to copolymerize CZ with 3MeT electrochemically, so that the as-formed copolymers could have the advantages of both P3MeT and PCZ.

In this study, CZ and 3MeT were copolymerized successfully by the electrochemical oxidation of the monomer mixtures in BFEE. The electrochemistry of PCZ, P3MeT, and copolymers of CZ with 3MeT was studied. In addition, the thermal stability, spectroscopic properties, conductivity, and morphology of the copolymers were investigated in detail.

EXPERIMENTAL

Materials

BFEE (Beijing Changyang Chemical Plant, Beijing, China) was distilled and stored at -20°C before use. CZ (Shanghai Chemical Plant, Shanghai, China) and 3MeT (99%; Acros Organics, Fair Lawn, NJ) were used directly. Sulfuric acid (98%) and 25% ammonia, made by Jinan Chemical Reagent Co. (Jinan, China), were used as received.

Electrochemical experiments

The electrochemical examinations and syntheses were performed in a one-compartment, three-electrode cell with the use of a model 263 potentiostat/galvanostat (EG&G Princeton Applied Research, Oak Ridge, TN) under computer control at room temperature. The cyclic voltammetry (CV) experiments were investigated with a platinum electrode with a diameter of 0.05 mm that was polished and cleaned

with water and acetone successively before each examination. The counter electrode was stainless steel wire. To obtain the freestanding film, stainless steel plates with surface areas of 10 and 12 cm^2 were used as the working electrode and counter electrode, respectively. The stainless steel electrodes were polished with abrasive paper (1500 mesh) and then washed with acetone before each examination. The copolymers were deposited on indium tin oxide coated glass for ultraviolet-visible (UV-vis) spectroscopy measurements. All potentials were referred to a saturated calomel electrode (SCE).

All the polymers were grown in pure BFEE. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during the experiments. For spectral analysis, the polymers were dedoped with 25% ammonia for 3 days and then washed repeatedly with water and acetone. At last, they were dried *in vacuo* at 60°C for 2 days.

Characterization

The conductivity of the as-formed polymer films was measured with the conventional four-probe technique. UV-vis spectra were taken with a Cary 500 UV-vis/near-infrared spectrophotometer (Nicolet, Waltham, MA). Infrared spectra were recorded with a Nicolet 510P FTIR spectrometer with KBr pellets. The thermogravimetric analysis (TGA) was performed with a Netzsch TG209 thermal analyzer (Bavaria, Germany). All thermal analyses were performed under a nitrogen stream in the temperature range of 303–1073 K at a heating rate of 10 K/min. Scanning electron microscopy (SEM) measurements were taken with a JEOL JSM-6700F scanning electron microscope (Tokyo, Japan).

RESULTS AND DISCUSSION

Electrochemical copolymerization

To ensure the copolymerization of CZ and 3MeT in BFEE, the electrochemical experiments were classified into different groups on the basis of the feed ratios of the two monomers. The results obtained from the aforementioned experiments indicated that the oxidation potential of 3MeT was much higher than that of CZ ($\Delta E > 0.4\text{ V}$), where ΔE is the difference of the oxidation potentials between CZ and 3MeT. It is well known that the successful electrochemical copolymerization of different monomers is due to the fact that the oxidation potentials of the monomers are close to each other.³⁸ From this point, it seems that it is almost impossible to achieve the electrochemical copolymerization of CZ and 3MeT. To realize the copolymerization successfully, we tried the strategy of the diffusion method established

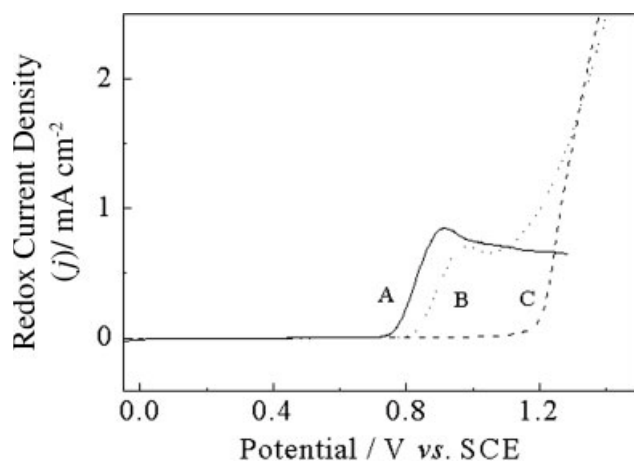


Figure 1 Anodic polarization curves of (A) 0.005 mol/L CZ, (B) 0.1 mol/L 3MeT, and (C) 0.005 mol/L CZ and 0.1 mol/L 3MeT in BFEE. The potential scanning rate was 20 mV/s.

by Kuwabata et al.³⁹ According to the diffusion method, this copolymerization reaction oxidizes CZ under diffusion-limited conditions under which 3MeT oxidation occurs, and this implies that the copolymerization is feasible. For this reason, after a series of experiments with different feed ratios of CZ and 3MeT, the concentration of CZ was chosen to be 0.005 mol/L, whereas that of 3MeT was 0.1 mol/L.

The anodic polarization curves taken in BFEE solutions at a potential scanning rate of 20 mV/s are given in Figure 1. The background electrolyte is electrochemically silent in the whole potential range. As predicted theoretically,⁴⁰ the oxidation of the substrate has a significant influence on the polymerization potential. There is an oxidation process of the stainless steel electrode before the electropolymerization process. This process causes the formation of a passive layer on the electrode surface. The formed passive film has two roles: protection of the electrode against dissolution and generation of a suitable surface for the deposition of the conducting polymer. Thus, the passivated substrate electrode has no significant effect on the nature of the prepared polymers.⁴¹ The oxidation onset of CZ was initiated at 0.75 V [Fig. 1(A)], and that of 3MeT was initiated at 1.15 V [Fig. 1(B)]. When a current potential curve was taken in BFEE containing 0.005 mol/L CZ and 0.1 mol/L 3MeT, curve B was obtained, which can be regarded as the superposition of curves A and C.³⁹ However, curves A and C cannot add up strictly to curve B. This may be partly due to some changes in the electrochemical environment caused by the successive deposition of the two monomers during the anodic polarization^{38,42} or partly due to the influence of the low electric conductivity accompanied by the incorporation of CZ units into the copolymer chain. In addition, the fact that the oxidation potential (ca. 0.88 V) of the mixture of CZ and

3MeT was between those of the two monomers implied that the two monomers were oxidized alternately and that the copolymer chains were composed of alternating CZ and 3MeT units, which also indicated the occurrence of the copolymerization.

The successive cyclic voltammograms of 0.005 mol/L CZ, 0.1 mol/L 3MeT, and a mixture of the two monomers, taken in pure BFEE at a potential scanning rate of 50 mV/s, are illustrated in Figure 2. As the CV scan continued, a polymer film was also formed on the working electrode surface. PCZ was reduced and oxidized between 0.45 and 0.53 V [Fig. 2(A)]. On the other hand, P3MeT was reduced and oxidized between 0 and 0.72 V. The increase in the redox wave currents implied that the amount of the polymer on the electrode increased. There was a negative shift of the cyclic voltammograms for the electropolymerization of 3MeT, whereas this was absent for CZ. The potential shift of this maximum provided information about the increase in the electrical resistance in the polymer film and the overpotential needed to overcome that resistance.⁴³ The cyclic voltammograms of 3MeT showed a pronounced hysteresis,⁴⁴ that is, a considerable difference between the anodic and cathodic peak potentials. The peak potential shift of the cyclic voltammograms of the conducting polymer can be hardly explained by conventional kinetic limitations such as ion diffusion or interfacial charge-transfer processes. The main reasons accounting for this phenomenon are

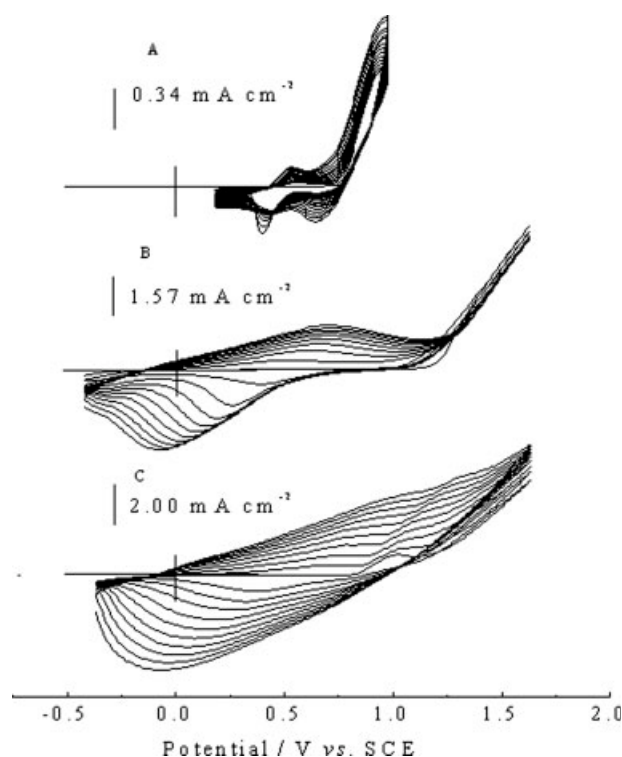


Figure 2 Cyclic voltammograms of (A) 0.005 mol/L CZ, (B) 0.1 mol/L 3MeT, and (C) 0.005 mol/L CZ and 0.1 mol/L 3MeT in BFEE. The potential scanning rate was 50 mV/s.

usually as follows:⁴⁵ slow heterogeneous electron transfer, effects of the local rearrangements of polymer chains, slow mutual transformations of various electronic species, and electronic charging of a sum of two interfacial exchanges corresponding to the metal/polymer and polymer/solution interfaces. In particular, the main reason for the differences in the cyclic voltammograms between P3MeT and PCZ could be the higher concentration of 3MeT (0.1 mol/L) together with the high doping level of P3MeT (28%).⁴⁶ The high concentration led to the rapid growth of P3MeT film during the potentiodynamic process. During the doping/dedoping, the anionic exchange in and out of the P3MeT film was slower than that of the CV scanning. Therefore, the great potential shift of P3MeT could be clearly seen, as shown in Figure 2. On the contrary, the concentration of CZ in the solution was relatively low. The amount of PCZ on the electrode per CV cycle was very limited. The exchange of the doping anions in and out of the PCZ films was in good agreement with the potential scanning. Therefore, no potential shift of the PCZ films was observed. When the cyclic voltammograms were taken in the electrolytic solutions containing 0.005 mol/L CZ and 0.1 mol/L 3MeT, great differences in the cyclic voltammograms could be easily observed [Fig. 2(C)]. In sharp contrast to the pure monomers, the oxidation potential of the mixture shifted positively, whereas the reduction potential of the mixture was between those of the two monomers. The evolution of a new wave at potentials different from the potentials of both pure CZ and 3MeT suggested the formation of a copolymer.⁴⁷ In addition, the shape of Figure 2(C) is similar to that of Figure 2(B), and this may be ascribable to the higher concentration of 3MeT in this medium.

Electrochemistry of the copolymer films

To investigate the electrochemical stability, the electrochemical behaviors of the PCZ, P3MeT, and copolymers of CZ and 3MeT deposited electrochemically from BFEE were studied in concentrated sulfuric acid (Fig. 3). As shown in Figure 3(A), the redox current densities decreased rapidly cycle by cycle during CV, and this implied that the stability of the PCZ films in sulfuric acid was not very good. In sharp contrast to the PCZ films, the steady-state cyclic voltammograms of P3MeT films presented broad and very stable anodic and cathodic peaks [Fig. 3(B)], which could be cycled repeatedly without obvious decomposition in sulfuric acid, indicating the high stability of the P3MeT films. For the copolymer prepared at 1.3 V, there was a new couple of the anodic/cathodic current peak, which was different from those of PCZ and P3MeT, indicating that a new polymer was obtained. In addition, the decomposition of the copolymer was not obvious in con-

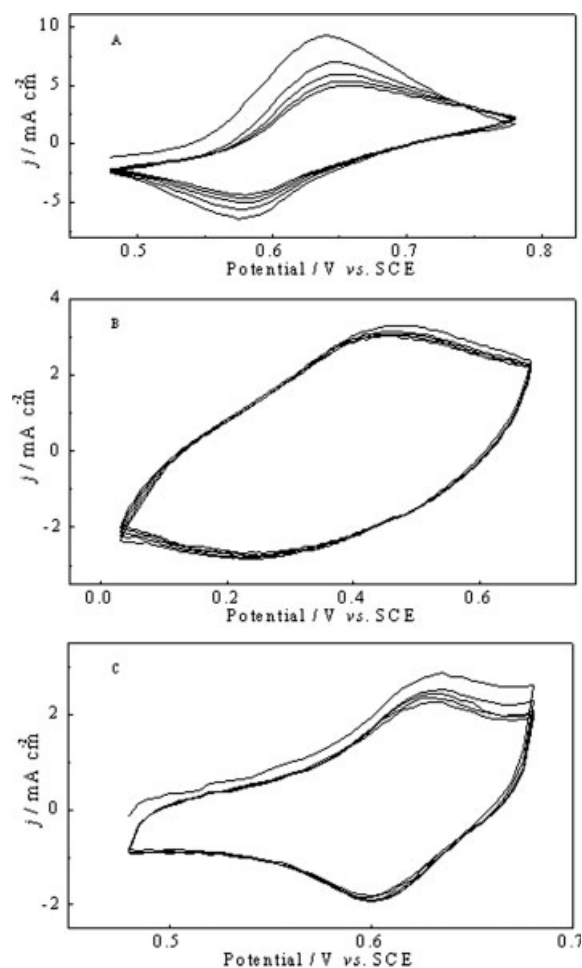


Figure 3 Cyclic voltammograms recorded in concentrated sulfuric acid of (A) PCZ, (B) P3MeT, and (C) a copolymer (at 1.3 V) prepared from BFEE. The potential scanning rate was 50 mV/s.

trast to PCZ, and this could be ascribed to the incorporation of 3MeT units into the copolymer chain. Therefore, it could be reasonably concluded that the copolymer film obtained from BFEE showed higher electrochemical stability than PCZ.

The electrochemical properties of copolymers obtained from BFEE solutions containing 0.005 mol/L CZ and 0.1 mol/L 3MeT at different potentials were also investigated. The cyclic voltammograms of the copolymers obtained at potentials ranging from 1.1 to 1.6 V were recorded in pure BFEE, as shown in Figure 4(A–F). The redox curve values of the copolymers are listed in Table I. Table I shows that the cathodic potentials shifted more negatively with an increase in the applied potentials, whereas the anodic potentials shifted positively along with the increases in the applied potentials. Moreover, according to the cyclic voltammograms in Figure 4, the difference in the peak current density was also interesting. With the increase in the applied potentials, the anodic/cathodic curve current densities increased, and this implied that there was a distinct

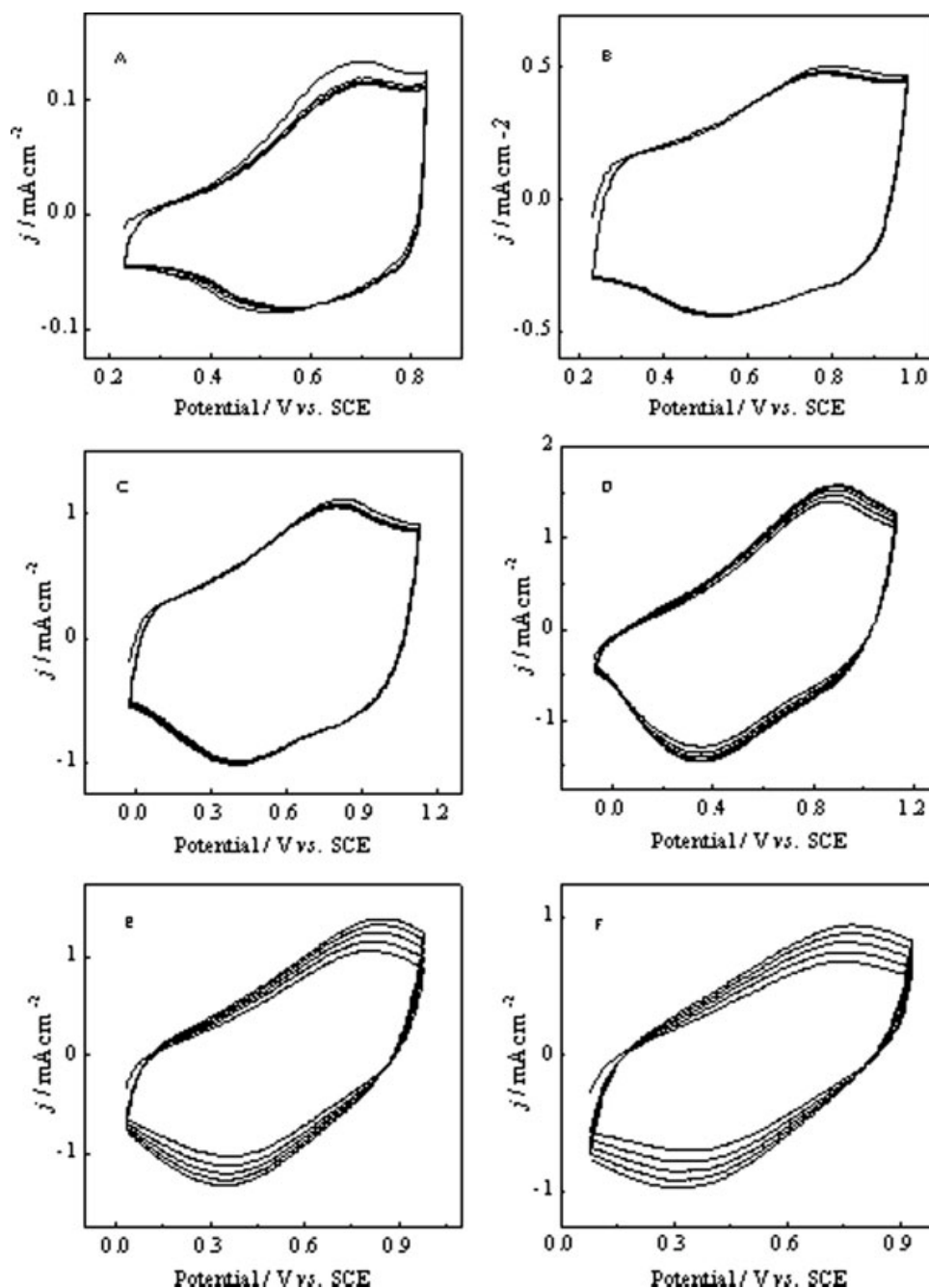


Figure 4 Cyclic voltammograms recorded in monomer-free BFEE of copolymers prepared at (A) 1.1, (B) 1.2, (C) 1.3, (D) 1.4, (E) 1.5, and (F) 1.6 V. The potential scanning rate was 50 mV/s.

capacitive feature of the charge storage due to the incorporation of more 3MeT units into the copolymers.⁴⁸ The higher the applied potential was, the more 3MeT units were incorporated into the copolymers, in accordance with the literature.³⁰ However, when the applied potential exceeded 1.3 V, the copolymer underwent obvious decomposition. This may have been due to the destruction of the conjugated structure of the copolymer at much higher potentials.³⁸ In addition, the stabilities of the polymer films were different (Figs. 3 and 4), and this could be ascribed to the different electrolyte

solutions in the corresponding experiments. The electrolyte solutions were concentrated sulfuric acid in Figure 3 and monomer-free BFEE in Figure 4, respectively. This also indicated that the electrolyte solutions had significant effects on the electrochemical stability of the films. PCZ showed significant decomposition in concentrated sulfuric acid [Fig. 3(A)], whereas P3MeT was very stable [Fig. 3(B)]. The copolymer showed good stability in concentrated sulfuric acid [Fig. 3(C)]. The cyclic voltammograms of the bilayer (P3MeT-PCZ composite), prepared by the successive polymerization of

TABLE I
Redox Peak Values and Conductivities of Copolymers Prepared from BFEe Containing 0.005 mol/L CZ and 0.1 mol/L 3MeT

Polymerization potential (V)	1.1	1.2	1.3	1.4	1.5	1.6
Polymerization time (s)	100	100	100	100	100	100
Anodic potential (V)	0.70	0.72	0.83	0.88	0.83	0.75
Cathodic potential (V)	0.56	0.52	0.42	0.35	0.34	0.32
Anodic current density (mA/cm ²)	0.12	0.48	1.1	1.55	1.40	1.6
Cathodic current density (mA/cm ²)	-0.09	-0.45	-1.03	-1.47	-1.34	-1.0
Conductivity (S/cm)	0.42	1.57	24.21	6.77	0.37	0.29

The conductivities of PCZ and P3MeT were 7.0×10^{-3} and 65.22 S/cm, respectively.

P3MeT and PCZ, were only the sum of the voltammograms of P3MeT and PCZ, as shown in Figure 5. This was quite different from those of the copolymers, further confirming the occurrence of copolymerization.⁴⁹

Structural characterization

During the potentiostatic process, the originally colorless solutions darkened step by step with the polymerization. This indicated that soluble oligomers might have formed during anodic oxidation. With the propagation of the polymerization, partly soluble oligomers became insoluble and were deposited on the working electrode with the elongation of the polymer main chain. However, there were still some oligomers, which diffused from the electrode into the bulk solution. As a result, the color of the bulk solution darkened. The PCZ film was transparent and colorless in the dedoped state and dark green in the doped form; this was similar to the literature.⁵⁰⁻⁵³ The P3MeT film changed its color from transparent red in the dedoped state to navy blue in the doped state.³⁰ For the copolymer, its color varied from navy blue in the doped state to a darkish color in the dedoped state.

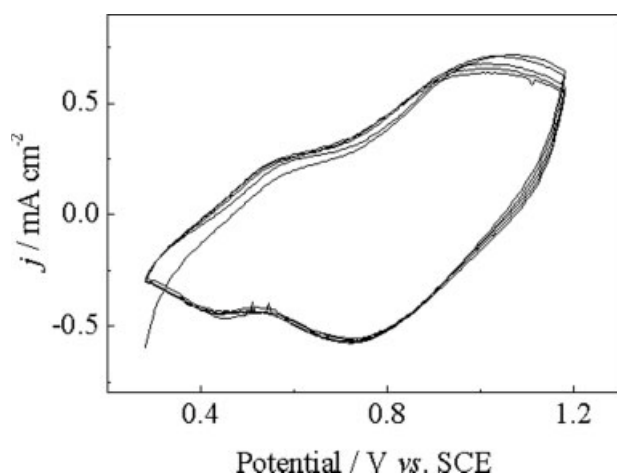


Figure 5 Cyclic voltammograms recorded in monomer-free BFEe of a bilayer (P3MeT-PCZ composite). The potential scanning rate was 25 mV/s.

The UV-vis spectra of pure PCZ, P3MeT, and copolymer films deposited at different potentials are shown in Figure 6. The broadening of the absorbance of the polymer in comparison with the monomers implied the wide molar mass distribution of the as-prepared films during the electrosyntheses. The P3MeT film showed a much broader absorption with a maximum at 482 nm. For the PCZ film, there was a slight absorption at 369 nm with a shoulder around 408 nm. Similarly to pure PCZ and P3MeT, the spectrum of the copolymer showed characteristic absorptions for both PCZ and P3MeT [Fig. 6(C,D)]. However, there was a slight redshift of the main absorption of the copolymer films in comparison with that of pure PCZ due to the incorporation of 3MeT units, further confirming the occurrence of copolymerization. Moreover, there was a small increase in the absorption in the visible region with the increase in the applied potential during copolymerization.

As-formed PCZ, P3MeT, and copolymers were all insoluble in strongly polar solvents such as water and also insoluble in weakly polar or nonpolar solvents such as acetone, tetrahydrofuran, and acetonitrile; this made it hard to perform more complete characterizations.

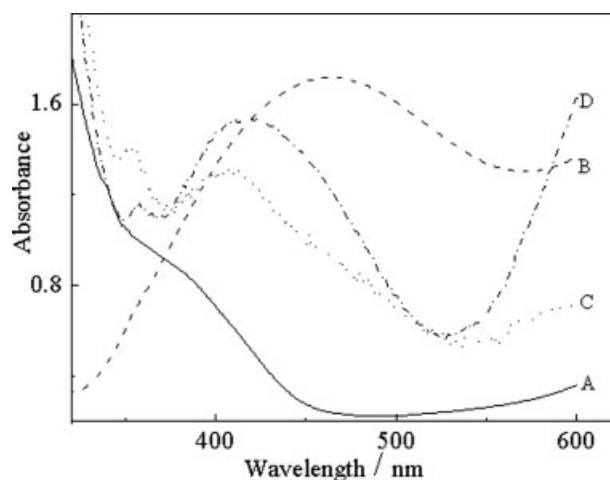


Figure 6 UV-vis spectra of (A) PCZ, (B) P3MeT, (C) a copolymer (1.3 V), and (D) a copolymer (1.6 V) prepared from BFEe.

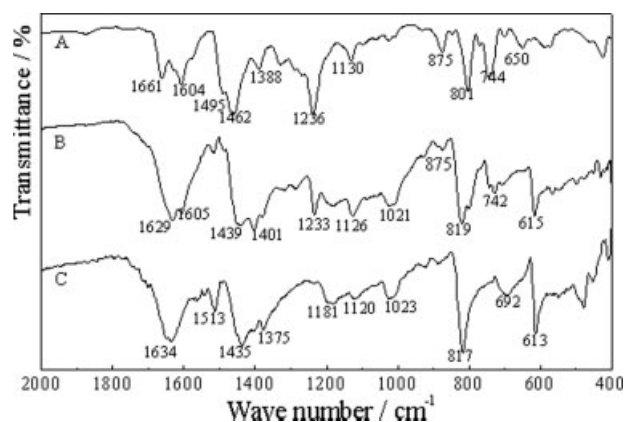


Figure 7 FTIR spectra of (A) PCZ, (B) a copolymer, and (C) P3MeT obtained from BFEE after a treatment with 25% aqueous ammonia for 3 days.

Infrared spectra can provide evidence for the occurrence of copolymerization, especially for those insoluble and infusible. P3MeT, PCZ, and copolymers prepared potentiostatically from BFEE containing 0.005 mol/L CZ and 0.1 mol/L 3MeT at 1.3 V were analyzed with FTIR spectroscopy, as shown in Figure 7. The bands of PCZ located at 875 and 801 cm^{-1} , evidence for the presence of a trisubstituted benzene ring,⁵⁴ indicated the occurrence of the polymerization on the benzene ring. These bands could also be found for the copolymer [Fig. 7(B)]. The bands at 1236 cm^{-1} [Fig. 7(A)] were related to the C—C deformation of PCZ.⁵⁵ The band at 744 cm^{-1} was assigned to the characteristic bands of the benzene ring, which could also be observed in Figure 7(B). In the spectrum of pure P3MeT [Fig. 7(C)], the bands at 1634 and 1120 cm^{-1} , originating from the stretching modes of C=C in the thiophene ring,⁵¹ and the band at 817 cm^{-1} were assigned to the out-of-plane C—H band, which could be found for the copolymer. As shown in Figure 7(C), the characteristic bands of the 2,5-disubstituted 3MeT unit clearly appear: the aromatic ring stretching bands at 1513 cm^{-1} . The bands located at about 1375 and 1435 cm^{-1} were assigned to the deformation of the methyl group.^{53,56} The narrow peak at 613 cm^{-1} of the P3MeT spectrum was the characteristic absorption of the C—S bond, which was also located in the copolymer. On the basis of the previous discussion, the characteristic peaks of pure P3MeT and pure PCZ could be found in the spectrum of the copolymer [Fig. 7(B)]. All these features implied that the copolymerization happened during the potentiostat electropolymerization of CZ and 3MeT, and this was consistent with the results of CV.

Thermal analysis

To investigate the thermal stability of the copolymers of 3MeT and CZ, the thermal properties of

P3MeT, PCZ, and their copolymers obtained at 1.3 V were investigated, as shown in Figure 8. PCZ started to lose weight when the temperature reached 640 K, whereas the prominent decomposition of P3MeT happened at about 735 K. Their corresponding maximum decomposition rates occurred at 685 and 790 K for PCZ and P3MeT, respectively. This indicated that the thermal stability of P3MeT was better than that of PCZ. The copolymer obtained at 1.3 V underwent degradation at about 700 K, which was higher than that of PCZ. This could be ascribed to the incorporation of 3MeT units. On the other hand, because of the higher concentration of 3MeT in this medium, the thermal properties of the obtained copolymers were similar to those of P3MeT. All the aforementioned results implied that the incorporation of 3MeT units into the polymer contributed to the improvement of the thermal properties of PCZ.

Conductivity and morphology

The conductivity of PCZ, P3MeT, and the copolymers prepared with different polymerization potentials are listed in Table I. Pure P3MeT exhibited excellent conductivity in this study, up to 65.22 S/cm, whereas the conductivity of PCZ was about 7.0×10^{-3} S/cm. The conductivities of the copolymers were between those of pure PCZ and P3MeT. This indicated that the insertion of 3MeT units into PCZ was helpful for improving the conductivity of PCZ, and this may be beneficial for extending the applications of PCZ. In addition, among the copolymers under different potentials, the polymer electrosynthesized potentiostatically at 1.3 V showed the highest conductivity, 24.21 S/cm. This was in accordance with the electrochemical analysis results. Therefore, 1.3 V was the best potential suitable for the electropolymerization of CZ and 3MeT.

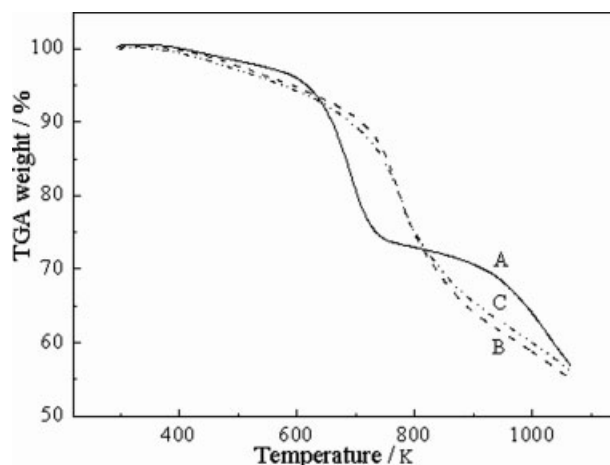


Figure 8 TGA curves of (A) PCZ, (B) P3MeT, and (C) a copolymer (1.3 V) from BFEE after a treatment with 25% aqueous ammonia for 3 days.

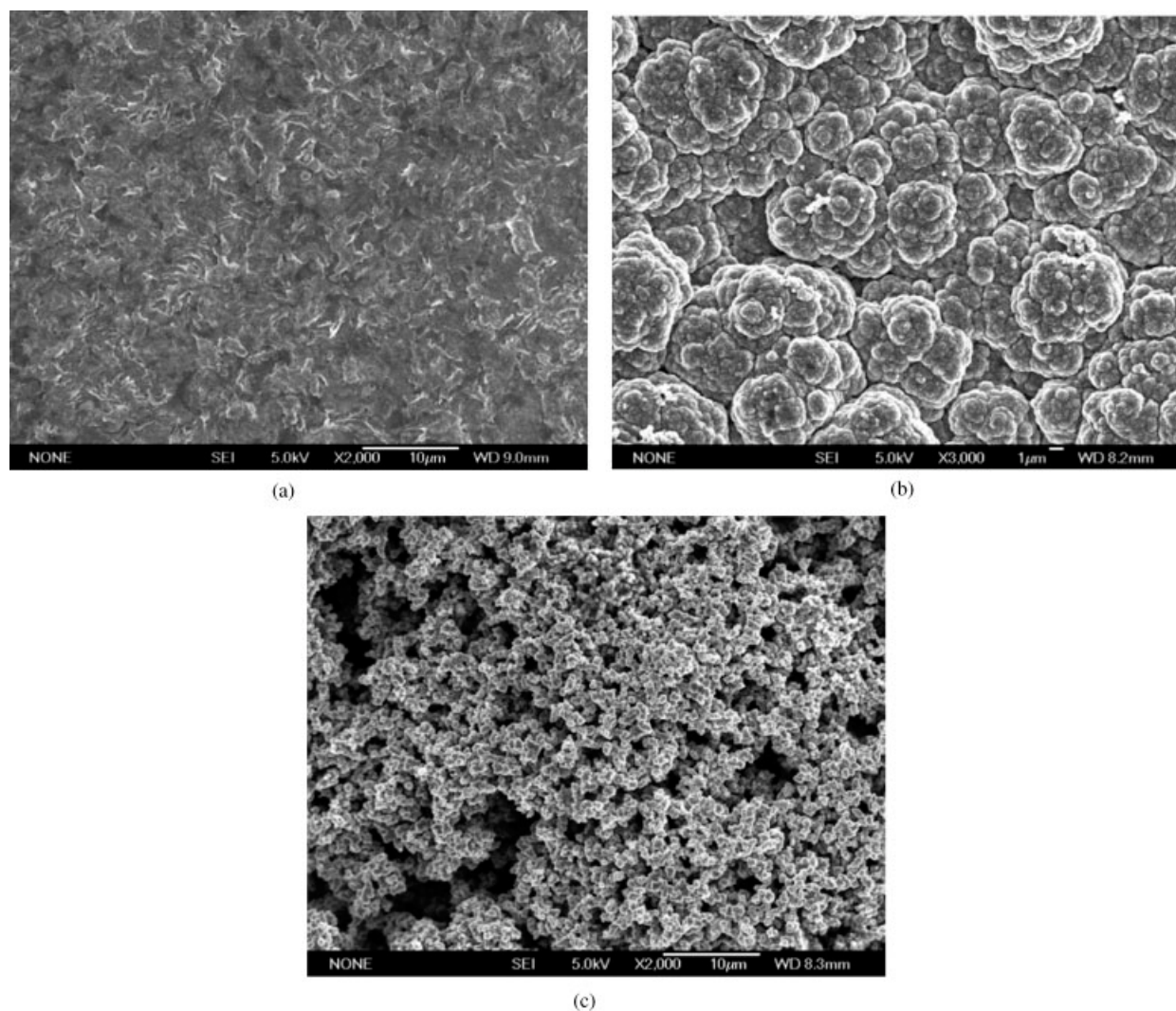


Figure 9 SEM images of (a) PCZ, (b) P3MeT, and (c) a copolymer prepared at 1.3 V from a BFEE solution containing 0.005 mol/L CZ and 0.1 mol/L 3MeT.

The properties of the conducting polymers were strongly dependent on their morphology and structure. Therefore, the SEM micrographs of PCZ, P3MeT, and their copolymer prepared at 1.3 V were examined, as shown in Figure 9. In this case, the morphology of pure PCZ appeared branched and dendritic [Fig. 9(A)], whereas the morphology of pure P3MeT was very regular, with a growth of aggregates shaped as blossoms [Fig. 9(B)]. The morphology of the copolymer obtained at 1.3 V showed a grain structure, as shown in Figure 9(C).

CONCLUSIONS

The electrochemical copolymerization of CZ and 3MeT was successfully realized in BFEE containing 0.005 mol/L CZ and 0.1 mol/L 3MeT by the potentiostatic method. The influence of the polymerization

potential on the properties of as-formed copolymers was studied in detail, and 1.3 V was tested to be the best for the electrocopolymerization of CZ and 3MeT. The copolymer showed good redox activity, capacitive properties, electrical conductivity, and thermal stability. These copolymer properties could extend the applications of both PCZ and P3MeT.

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