

Electrodeposition of Free-Standing Poly(*o*-dihydroxybenzene-*co*-3-methylthiophene) Films with Tunable Fluorescence Properties

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ABSTRACT: Electrochemical copolymerization of *o*-dihydroxybenzene (*o*DHB) and 3-methylthiophene (3MeT) was successfully achieved in boron trifluoride diethyl etherate by direct anodic oxidation of the monomer mixtures, although the oxidation potentials of *o*DHB and 3MeT were quite different. The influence of the applied polymerization potential on the synthesis of the copolymers was investigated. The higher applied potential favored the incorporation of 3MeT units into the copolymers. The structure and properties of the copolymers were investigated with UV-vis spectroscopy, fluorescence spectroscopy,

FTIR spectroscopy, and thermal analysis. The novel copolymers had many advantages, including good redox activity, good thermal stability, and high electrical conductivity. Additionally, the copolymers fluorescence properties that were tunable through changes in the feed ratio of the monomer mixtures. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3273–3281, 2010

Key words: conducting polymers; copolymerization; electrochemistry

INTRODUCTION

The pursuit of novel conducting polymers is still one of the main goals in the syntheses and applications of conducting polymers. Poly(3,4-ethylenedioxythiophene) has attracted much attention among conducting polymers because of its high conductivity, good processing ability, good mechanical properties, and nice environmental stability.¹ Poly(1,2-methylenedioxybenzene), a poly(3,4-ethylenedioxythiophene) derivative, is of great interest because of its good properties.² *o*-Dihydroxybenzene (*o*DHB) is a cheaper monomer, whose structure is similar to 1,2-methylenedioxybenzene (MDOB). Two electron-donating groups of —OH on benzene contribute to the polymerization of *o*DHB. As a novel conducting polymer, poly(*o*-dihydroxybenzene) (PoDHB), was successfully electrosynthesized by direct anodic oxidation of its monomer, *o*DHB, in pure boron trifluoride diethyl etherate (BFEE) with good fluorescence properties as a blue-light-emitting material together with good thermal

stability.³ However, it also has disadvantages because it is difficult to electrosynthesize high-quality, free-standing PoDHB films. It is well known that copolymerization is an effective method that can tune the properties of copolymers to be intermediate between those of the individual homopolymers. Therefore, a copolymer containing *o*DHB monomer units in the main backbone would be beneficial for extending the properties of PoDHB.

Poly(3-methylthiophene) (PMeT), an important derivative of polythiophene, has also been the subject of intense research because of its high electrical conductivity⁴ (close to 750 S/cm), high tensile strength, and good flexibility.⁵ High-quality, free-standing PMeT films with good properties can be easily produced by the direct anodic oxidation of 3-methylthiophene (3MeT) monomer in BFEE.⁶ Until now, 3MeT based copolymers have been prepared successfully by the electrochemical oxidation of mixtures of 3MeT with other corresponding monomers.^{7–15} To the best of our knowledge, the electrochemical copolymerization of *o*DHB with 3MeT in BFEE has not been reported so far. It was of interest to copolymerize *o*DHB with 3MeT.

In this study, *o*DHB and 3MeT were copolymerized successfully by the electrochemical oxidation of the monomer mixture in BFEE. The electrochemistry, thermal stability, spectroscopic properties, and

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electrical conductivity of PoDHB, PMeT, and their copolymers were studied in detail.

EXPERIMENTAL

Materials

BFEE (Beijing Changyang Chemical Plant, Beijing, China) was distilled and stored at -20°C before use (note that BFEE reacts violently and explosively with water, steam and moisture and, therefore, should be handled with care). *o*DHB (analytical grade; Tianjin Boding Chemicals Co., Ltd., Tianjin, China) and 3MeT (99%; Acros Organics, Fair Lawn, NJ) were used directly. Acetone (analytical grade) and dimethyl sulfoxide (DMSO; analytical grade) were products of Tianjin Boding Chemicals Co.

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. The typical electrolytic solutions were composed of BFEE with different feed ratios of the monomer mixtures. The electrochemical properties of these polymer films were characterized by cyclic voltammetry (CV) in a monomer-free BFEE solution. BFEE served not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte was needed. Before all measurements, the solutions were deaerated by a dry nitrogen stream. A nitrogen atmosphere had to be maintained over the solution, and all of the experiments were performed within a ice-water bath (0°C). A platinum electrode with a diameter of 0.5 mm was used as the working electrode, which was polished and cleaned with water and acetone successively before each examination. The counter electrode was stainless steel wire. For the electrodeposition of a large amount of polymer, stainless steel sheets 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. All potentials were referred to a saturated calomel electrode (SCE). The amount of polymer deposited on the electrode was controlled by the integrated charge passed through the cell. The polymers were scraped from the electrode after the electropolymerization and then washed with water and acetone to remove the electrolyte and monomer. The polymers were in a doped state. However, this would have had a negative effect on the oxidation state of the polymers. For spectral analysis, the polymers were dried in vacuum at 60°C for 2 days.

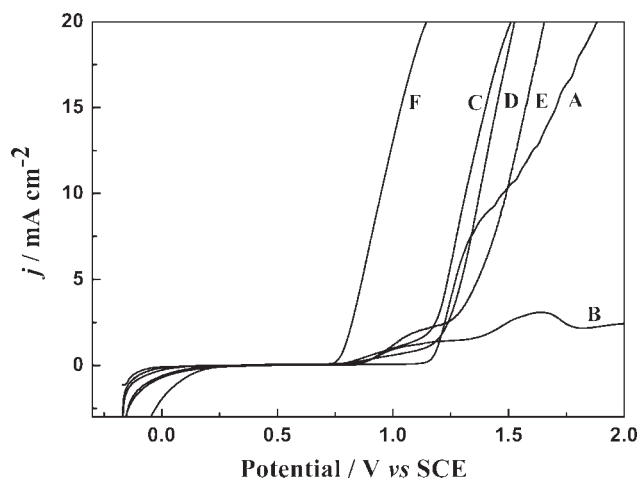


Figure 1 Anodic polarization curves of (A) 0.05 mol/L 3MeT, (B) 0.01 mol/L *o*DHB and 0.01 mol/L 3MeT, (C) 0.01 mol/L *o*DHB and 0.1 mol/L 3MeT, (D) 0.01 mol/L *o*DHB and 0.2 mol/L 3MeT, (E) 0.01 mol/L *o*DHB and 0.5 mol/L 3MeT, and (F) 0.2 mol/L *o*DHB in BFEE. The scanning rate was 20 mV/s.

Characterization

The electrical conductivity of as-formed polymer films was measured by the conventional four-probe technique. Ultraviolet–visible (UV–vis) spectra were taken with a PerkinElmer Lambda 900 UV–vis near-infrared spectrometer. Infrared spectra were recorded on a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer with KBr pellets. The fluorescence spectrum was determined with an F-4500 fluorescence spectrophotometer (Hitachi). $^1\text{H-NMR}$ spectra were recorded on a Bruker AV 400 NMR spectrometer, and CD_3SOCD_3 was used as the solvent. Thermogravimetric analysis was performed with a Pyris Diamond thermogravimetry (TG)/differential thermogravimetry (PerkinElmer) thermal analyzer. All thermal analyses were performed under a nitrogen stream in the temperature range 300–1100 K at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Electrochemical copolymerization

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 *o*DHB and 3MeT were quite different. To ensure the copolymerization of *o*DHB and 3MeT in BFEE, the electrochemical experiments were classified into different groups on the basis of the feed ratios of the two monomers. The anodic oxidation of 3MeT and *o*DHB was first examined. The onset oxidation potential (E_{ox}) of 3MeT in BFEE was tested to be 1.17 V [Fig. 1(A)], whereas E_{ox} for *o*DHB

TABLE I
Oxidation Potentials of *o*DHB, 3MeT, and the Monomer Mixtures in Pure BFEE

Sample	E_{ox} (V)
<i>o</i> DHB	0.73
<i>o</i> DHB/3MeT = 1 : 1	0.77
<i>o</i> DHB/3MeT = 1 : 10	0.80
<i>o</i> DHB/3MeT = 1 : 20	0.83
<i>o</i> DHB/3MeT = 1 : 50	0.88
3MeT	1.17

was 0.73 V [Fig. 1(F)]. E_{ox} of 3MeT was much higher than that of *o*DHB. It seemed that it was very difficult to achieve the electrochemical copolymerization of 3MeT and *o*DHB. To realize the copolymerization, we tried the diffusion method established by Kuwabata et al.¹⁶ The copolymerization strategy used in this study was the oxidation of *o*DHB under diffusion-limiting conditions at potentials where 3MeT oxidation took place. This implied that the copolymerization was feasible. To identify proper stoichiometries for the formation of the copolymer, various feed ratios of *o*DHB and 3MeT were tested. When the feed ratio of *o*DHB to 3MeT was 1 : 1, the initial E_{ox} of the monomer mixtures was 0.77 V [Fig. 1(B)], which was very close to that of *o*DHB. With an increase in 3MeT concentration, the E_{ox} values of the monomer mixtures shifted positively [Fig. 1(C–E)], and they were still closer to the oxidation potential of *o*DHB than to that of 3MeT, as shown in Table I. However, all of the E_{ox} values of the monomer mixtures were between those of the two monomers; this suggested that the two monomers might be oxidized together and that the copolymer chains were composed of both *o*DHB and 3MeT units.

The successive CVs of 3MeT, *o*DHB, and mixtures of the two monomers with various feed ratios in BFEE at a potential scanning rate of 100 mV/s are illustrated in Figure 2. As shown in Figure 2(A), as the potential scanning continued, a polymer film was formed on the electrode surface. The increases in the redox wave currents implied that the amount of the polymer on the electrode increased. The potential shift of the wave current maximum provided information about the increase in the electrical resistance in the polymer film and the overpotential needed to overcome the resistance. All of these phenomena indicated that a polymer film was formed on the electrode. Similar phenomena were also found during the CV of *o*DHB in BFEE [Fig. 2(F)]. PMeT could be oxidized and reduced between 0.73 and 0.07 V, and the CV diagrams of PMeT showed broad redox waves [Fig. 2(A)]. On the other hand, CV of *o*DHB showed broad redox waves with oxidation and reduction peaks at 0.61 and 0.47 V, respectively [Fig. 2(F)]. In particular, the main reason

for the differences in CV between PMeT and *o*DHB could have been the higher concentration of 3MeT together with the high doping level of PMeT.¹⁷ The

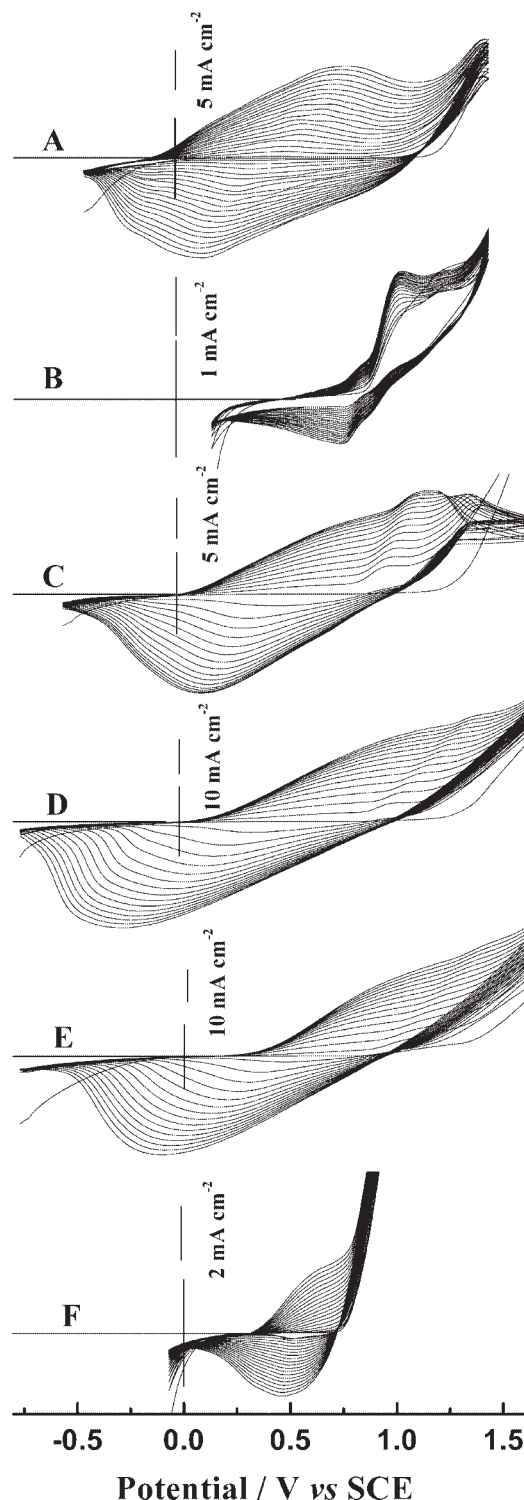


Figure 2 CV diagrams of (A) 0.05 mol/L 3MeT, (B) 0.01 mol/L *o*DHB and 0.01 mol/L 3MeT, (C) 0.01 mol/L *o*DHB and 0.1 mol/L 3MeT, (D) 0.01 mol/L *o*DHB and 0.2 mol/L 3MeT, (E) 0.01 mol/L *o*DHB and 0.5 mol/L 3MeT, and (F) 0.2 mol/L *o*DHB in BFEE. The scanning rate was 100 mV/s.

TABLE II
Oxidation and Reduction Potentials of PMeT, PoDHB,
and the Copolymers Measured in Pure BFEE

Sample	BFEE	
	E_{pa} (V)	E_{pc} (V)
3MeT	0.73	0.07
<i>o</i> DHB/3MeT = 1 : 1	1.01	0.74
<i>o</i> DHB/3MeT = 1 : 10	1.14	0.06
<i>o</i> DHB/3MeT = 1 : 20	1.31	-0.34
<i>o</i> DHB/3MeT = 1 : 50	1.29	-0.11
<i>o</i> DHB	0.61	0.47

E_{pa} and E_{pc} denote the potential of anodic and cathodic peak.

high monomer concentration led to the rapid growth of the PMeT film on the anode during the potentiodynamic process. The CV of monomer mixtures with various feed ratios were also recorded. In sharp contrast to homopolymers, the oxidation and reduction potentials of the copolymer shifted positively, as shown in Table II. The evolution of new waves at potentials different from those of homopolymers suggested the formation of copolymers.¹⁸ In addition to the increase in the 3MeT concentration, great changes were easily observed in the CV diagrams [Fig. 2(B–D)]. When the concentration of 3MeT increased to 0.5 mol/L, the CV curves of the copolymer were similar to that of PMeT, which implied that more 3MeT units were incorporated into the copolymer film [Fig. 2(E)].

Electrochemistry of the copolymer films

To investigate the electrochemical behavior, further studies were carried out for PoDHB, PMeT, and the copolymer films prepared with various feed ratios at constant applied potentials of 1.1, 1.2, and 1.2 V, respectively. The electrochemical properties of these polymer films were characterized by CV in a monomer-free BFEE solution, as shown in Figure 3. In BFEE, with a scanning rate of 50 mV/s, PMeT was oxidized and reduced from 0.61 V (anodic peak potential) to 0.34 V [cathodic peak potential; Fig. 3(A)], and PoDHB was oxidized and reduced from 1.02 to 0.15 V [Fig. 3(F)]. The copolymers films prepared with feed ratios of *o*DHB to 3MeT at 1 : 1 and 1 : 10 were oxidized and reduced from 1.23 to 0.70 V and from 0.53 to 0.28 V, respectively [Fig. 3(B,C)]; when the feed ratios of *o*DHB to 3MeT were 1 : 20 and 1 : 50, the copolymers were oxidized and reduced from 0.73 to 0.17 V and from 0.93 to 0.19 V, respectively [Fig. 3(D,E)]. The peak current densities were proportional to the potential scan rates (inset of Fig. 3), which indicated a redox couple fixing on the electrode.¹⁹ The polymer films were cycled repeatedly between the conducting (oxidized) and

insulating (neutral) states without significant decomposition of the materials in pure BFEE; this implied good stability of the polymer.

Structural characterization

During the potentiostatic process, the original colorless solution darkened gradually with the propagation of the polymerization. This indicated that soluble oligomers might have been formed during anodic oxidation. With the propagation of the polymerization, partly soluble oligomers became insoluble and were deposited on the working electrode. However, there were still some oligomers, which diffused from the electrode into the bulk solution. The polymer films deposited on the indium-tin-oxide (ITO) electrode were dedoped electrochemically. PoDHB was opaque and blue in the doped state. When dedoped, its color changed to light green. Dedoped PoDHB was soluble in common organic solvents, such as DMSO and tetrahydrofuran.³ The PMeT film changed color from transparent red in the dedoped state to navy blue in the doped state and was insoluble in all organic solvents.¹⁴ For the copolymers, their color varied from dark black in the doped state to a gray color in the dedoped state. The obtained copolymers in the doped state partly dissolved in common organic solvents such as DMSO.

The UV–vis spectra of the doped PMeT, PoDHB, and copolymer films deposited on the ITO electrode are shown in Figure 4. The doped PMeT film showed a much broader absorption from 650 to 860 nm with a peak at 756 nm [Fig. 4(A)], characteristic of the existence of charge carriers, such as polarons and bipolarons, in the doped state. In the course of the doping process, the originally filled valence band of PMeT became partially empty. The Fermi level lowered to the valence band, which ensured metallic behavior in PMeT. We expected that the more doped the PMeT was, the more empty the valence band would have become; as a consequence, the charge carrier concentration increased, and hence, the electrical conductivity also increased.⁵ The doped PoDHB film showed not only the absorption at 298 nm but also a strong absorption from 580 to 840 nm with a peak at 748 nm [Fig. 4(F)]. This wide peak was also assigned to the absorption of conductive species, such as polarons and bipolarons, on the main backbone of PoDHB in the doped state.³ Similarly to those of PoDHB and PMeT, the spectra of the copolymers showed characteristic absorptions for both PoDHB and PMeT and showed another characteristic absorption at 540 nm [Fig. 4(B–E)]. However, there was a slight redshift of the main absorption of the copolymer films in comparison

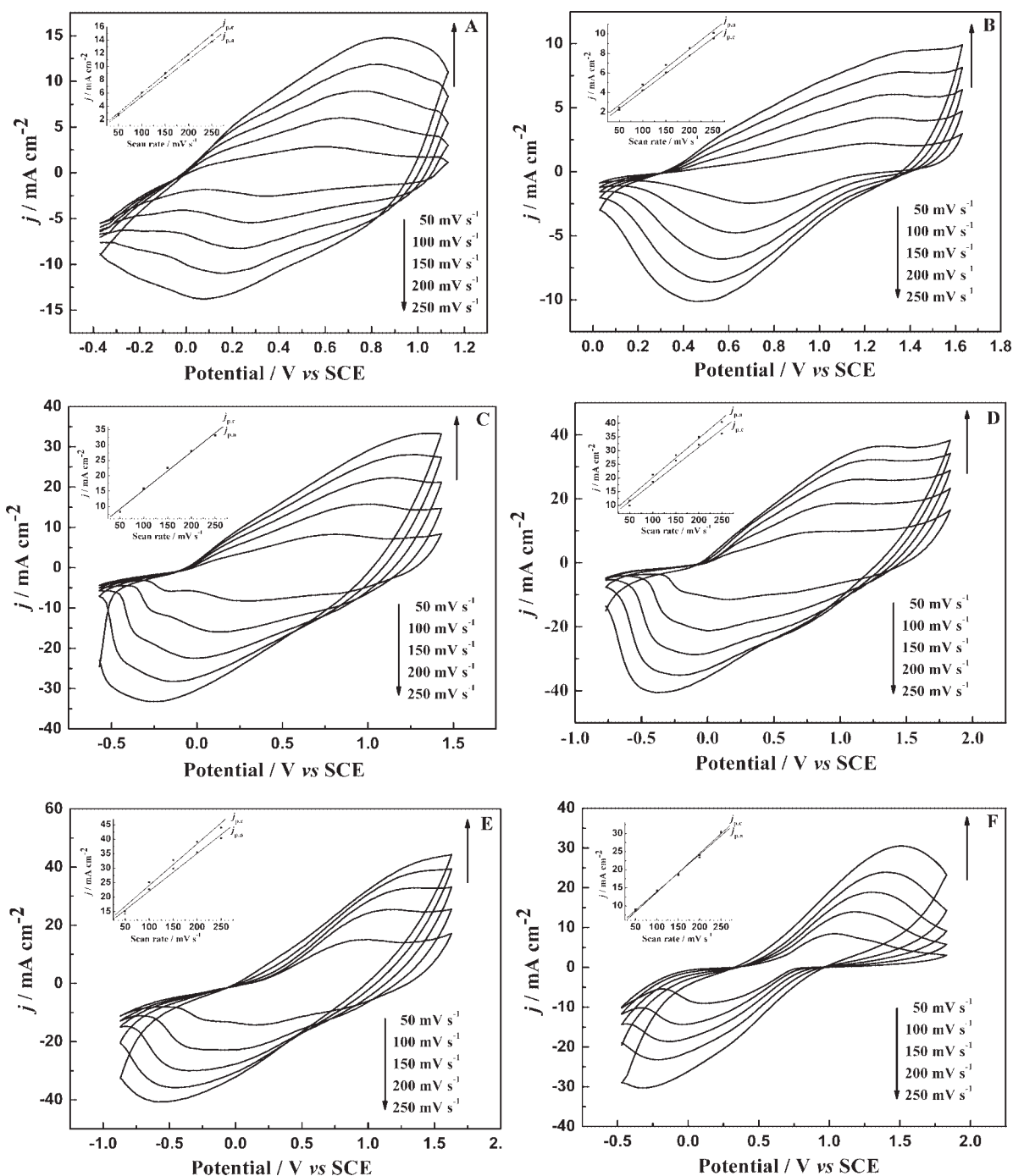


Figure 3 CV diagrams of (A) PMeT, (B) poly(*o*DHB-*co*-3MeT) (1 : 1), (C) poly(*o*DHB-*co*-3MeT) (1 : 10), (D) poly(*o*DHB-*co*-3MeT) (1 : 20), (E) poly(*o*DHB-*co*-3MeT) (1 : 50), and (F) PoDHB films recorded in BFEET. The scanning rates were 50, 100, 150, 200, and 250 mV/s. j is the current density; $j_{p,a}$ and $j_{p,c}$ are the anodic peak current density and the cathodic peak current density, respectively.

with that of PoDHB because of the incorporation of 3MeT units.

The FTIR spectra of the copolymers, in comparison with PMeT and PoDHB, are shown in Figure 5. In the spectrum of PMeT, the bands at 1615 and 1127 cm^{-1} originated from the stretching modes of C=C in the thiophene ring,²⁰ and the band at 771 cm^{-1} was assigned to the out-of-plane C-H band, which was found for the copolymers. As shown in

Figure 5(A), the characteristic bands of 2,5-disubstituted 3MeT units clearly appeared, the aromatic C-H stretching bands were located at 3115 cm^{-1} , and the band located at about 1407 cm^{-1} was assigned to the deformation of the methyl group.^{21,22} The narrow peak at 578 cm^{-1} of the PMeT spectrum was the characteristic absorption of the C-S bond, which was also found in the spectra of copolymers shifting to lower wave numbers. In the spectrum of

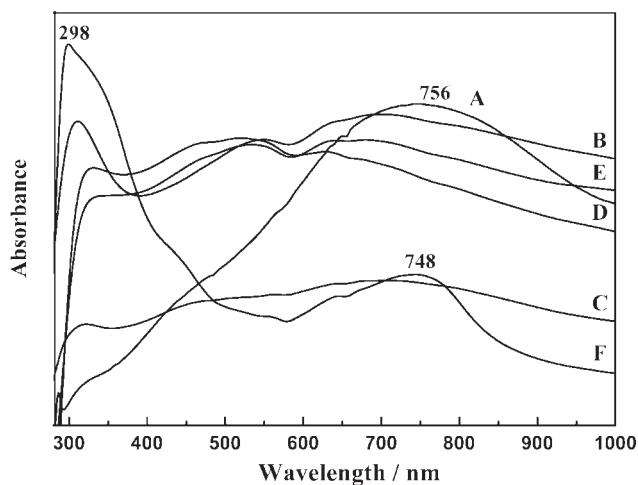


Figure 4 UV-vis spectra of (A) PMeT, (B) poly(*o*DHB-co-3MeT) (1 : 1), (C) poly(*o*DHB-co-3MeT) (1 : 10), (D) poly(*o*DHB-co-3MeT) (1 : 20), (E) poly(*o*DHB-co-3MeT) (1 : 50), and (F) PoDHB coated on an ITO electrode in the doped states.

PoDHB [Fig. 5(F)], the bands at 1721 and 856 cm^{-1} indicated a 1,2,4,5-substituted benzene ring. In copolymers, a band at 1721 cm^{-1} was also found. The bands from 1622 to 1376 cm^{-1} showed the vibrations of the backbone of benzene. These bands were also found for the copolymer [Fig. 5(B,E)]. However, as shown in Figure 5(C,D), the bands from 1622 to 1376 cm^{-1} showed a little shift. The bands from 1234 to 1152 cm^{-1} showed the vibrations of C—O; the existence of the broad absorption at about 3248 cm^{-1} indicated that O—H still existed after polymerization, and these bands were also found in those of copolymers shifting to lower wave numbers [Fig. 5(B–E)]. All of these results imply that the copolymerization happened during the potentiostatic electropolymerization of *o*DHB and 3MeT and indicate that the copolymerization was successfully achieved and that the coupling reaction mainly occurred at the 2,5 position of 3MeT and the 4,5 position of *o*DHB (Scheme 1).

To further investigate the copolymer structure, the $^1\text{H-NMR}$ spectra of *o*DHB, 3MeT, and the copolymer were recorded. As shown in Figure 6(A), the spectrum of *o*DHB showed two groups of protons: 6.69–6.73 ppm (H-4, H-5) and 6.57–6.61 ppm (H-3, H-6). According to the spectrum of 3MeT [Fig. 6(C)], there were three groups of protons: one was located at 7.42 ppm (H-5); the other two groups were at 7.11 ppm (H-2) and 6.94 ppm (H-4). The proton lines of the copolymer [Fig. 6(B)] were broader than the corresponding proton lines of the *o*DHB [Fig. 6(A)] and 3MeT monomers [Fig. 6(C)] because of the wide molar mass distribution of the copolymer. Some new peaks appeared after copolymerization, and most of the peaks moved to a lower field, which was mainly because of the introduction of a higher conjugation

length in the copolymer main chain. As illustrated in Figure 6(B), there were three peaks in the copolymer spectra. The peak around 7.95 ppm (H-4) arose from the thiophene ring, and the other two peaks at 7.66–7.73 ppm (H-3, H-6) arose from the benzene ring of the *o*DHB units. On the basis of these considerations, together with the previous reports, the chemical structure of the copolymers were speculated, as shown in Scheme 1, to be in good accordance with the FTIR results.

Fluorescence properties

PoDHB is a good blue-light-emitting material,³ and the emission peak of the PMeT film was close to zero. On the other hand, PMeT has the advantage of easy electrodeposition as a free-standing film. With their advantages are combined, this novel copolymer, with properties intermediate between their individual properties, may meet the application of copolymers as good light emitting materials. The

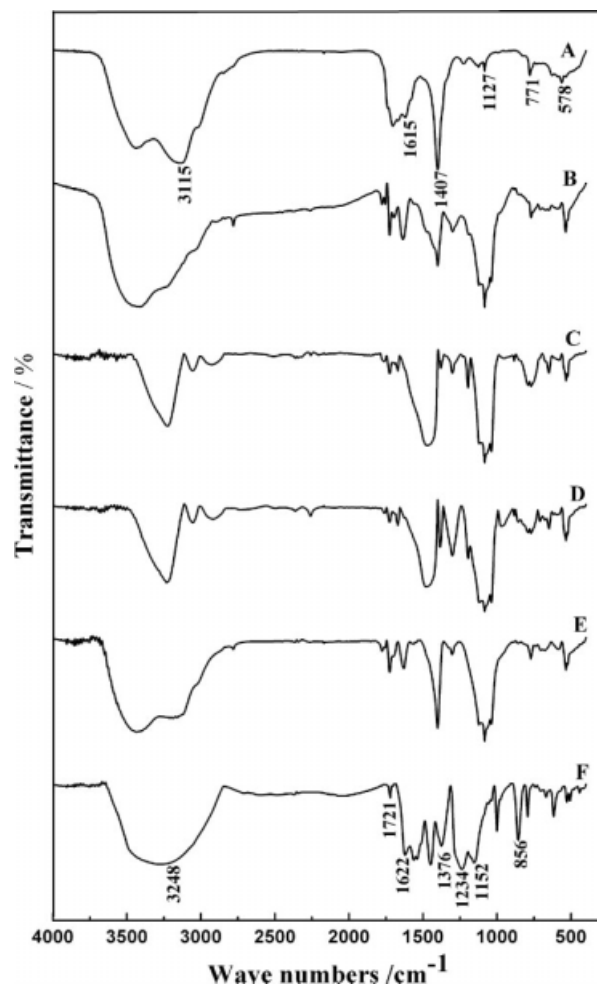
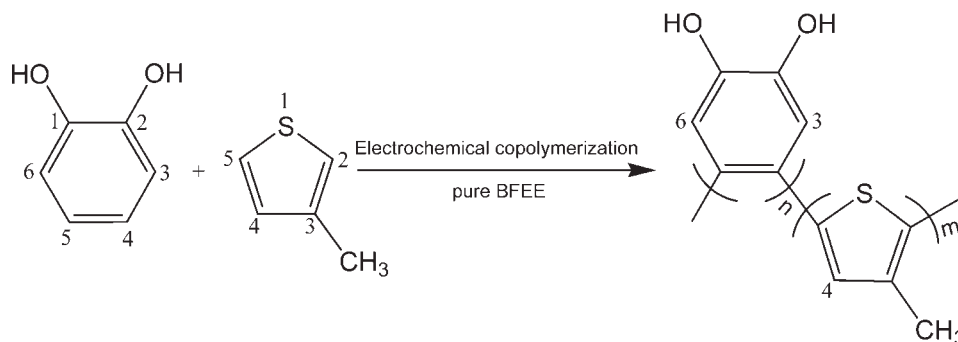


Figure 5 FTIR spectra of (A) PMeT, (B) poly(*o*DHB-co-3MeT) (1 : 1), (C) poly(*o*DHB-co-3MeT) (1 : 10), (D) poly(*o*DHB-co-3MeT) (1 : 20), (E) poly(*o*DHB-co-3MeT) (1 : 50), and (F) PoDHB.



Scheme 1 Possible chemical structure of the copolymers from *o*DHB and 3MeT.

fluorescence spectra of the doped PoDHB and copolymers prepared in BFEE were examined with DMSO as the solvent through the wavelength scans of emission. The emission maximum of PoDHB was mainly at 385 nm with two shoulders at 374 and 406 nm when excited at 350 nm [Fig. 7(A)]. The fluorescence spectra of the copolymer prepared with a monomer feed ratio of *o*DHB/3MeT = 1 : 1 showed an emission peak at 383 nm with one shoulder at 403 nm [Fig. 7(B)]. When the *o*DHB/3MeT ratio was 1 : 10, two emission peaks appeared at 523 and 383 nm with one shoulder at 403 nm [Fig. 7(C)]. For other feed ratios of *o*DHB to 3MeT such as 1 : 20 and 1 : 50, two emission peaks appeared at 383 and 523 nm [Fig. 7(D,E)]. The intensity of the emission peaks at 523 nm increased with increasing 3MeT concentration during the copolymerization [Fig. 7(B–E)], which was attributed to the incorporation of 3MeT units into the PoDHB chains. Upon irradiation with 365-nm UV light, the solutions of the copolymers showed different colors. When the feed ratio of *o*DHB to 3MeT was 1 : 1, the color of the solution turned to light blue in comparison to that of PoDHB. When the feed ratios of *o*DHB to 3MeT were 1 : 10, 1 : 20, and 1 : 50, the color of the solution gradually turned to yellow–green, as shown in Figure 8. On

the basis of these results, one could easily control the fluorescence properties of the copolymers by changing the feed ratio of the monomer mixtures.

Thermal analysis

The degradation behavior of conducting polymers is very important for their potential applications. PoDHB and PMeT have good thermal stability.^{3,15} Therefore, the thermal analyses of the copolymers were done by thermogravimetric analysis. All thermal analyses were performed under a nitrogen stream in the temperature range 300–1100 K with a heating grate of 10 K/min. As shown in Figure 9, poly(*o*-dihydroxybenzene-*co*-3-methylthiophene) [poly(*o*DHB-*co*-3MeT); 1 : 1] shows better thermal stability than the other copolymers with different feed ratios. The first decomposition started from 300 to 400 K, which was ascribed to the evaporation of water or other moisture trapped in the polymer. The second decomposition of the copolymer started from 400 to 550 K. This weight loss was attributed to the degradation of the skeletal

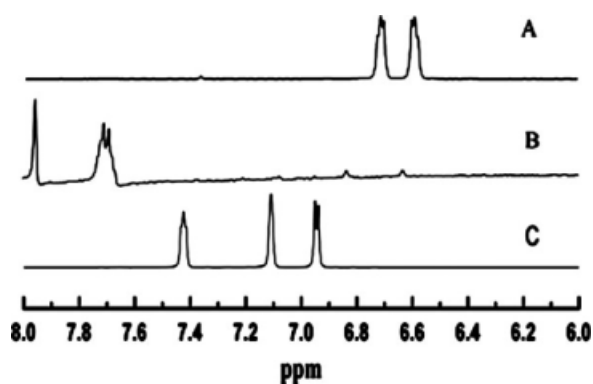


Figure 6 ¹H-NMR spectra of (A) *o*DHB, (C) 3MeT, and (B) the copolymer prepared from a pure BFEE solution containing 0.01 mol/L *o*DHB and 0.1 mol/L 3MeT at 1.2 V versus SCE (solvent: CD₃SOCD₃).

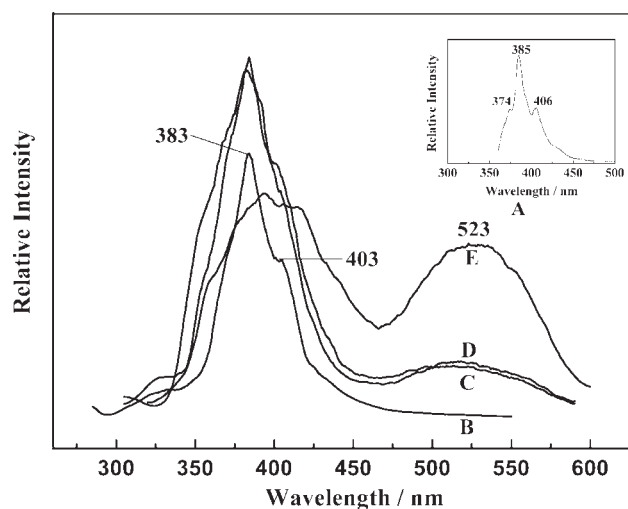


Figure 7 Fluorescence spectra of (A) PoDHB, (B) poly(*o*DHB-*co*-3MeT) (1:1), (C) poly(*o*DHB-*co*-3MeT) (1:10), (D) poly(*o*DHB-*co*-3MeT) (1:20), and (E) poly(*o*DHB-*co*-3MeT) (1:50) (solvent: DMSO).

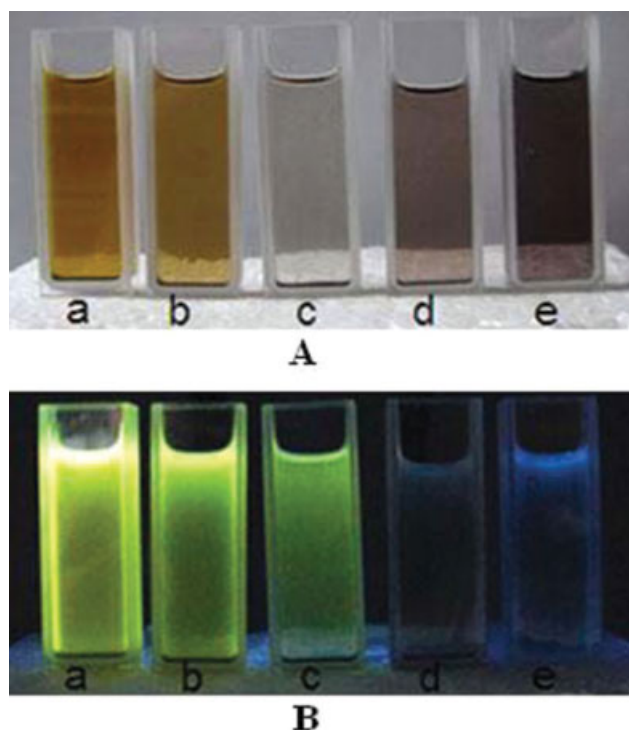


Figure 8 (A) Photographs of (a) poly(*o*DHB-*co*-3MeT) (1 : 50), (b) poly(*o*DHB-*co*-3MeT) (1 : 20), (c) poly(*o*DHB-*co*-3MeT) (1 : 10), (d) poly(*o*DHB-*co*-3MeT) (1 : 1), and (e) PoDHB dissolved in DMSO under natural light. (B) Photographs of (a) poly(*o*DHB-*co*-3MeT) (1 : 50), (b) poly(*o*DHB-*co*-3MeT) (1 : 20), (c) poly(*o*DHB-*co*-3MeT) (1 : 10), (d) poly(*o*DHB-*co*-3MeT) (1 : 1), and (e) PoDHB dissolved in DMSO under UV irradiation (365 nm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolymer main backbone. Other small decompositions occurred between 550 and 1060 K, possibly because of some oligomers that decomposed from the

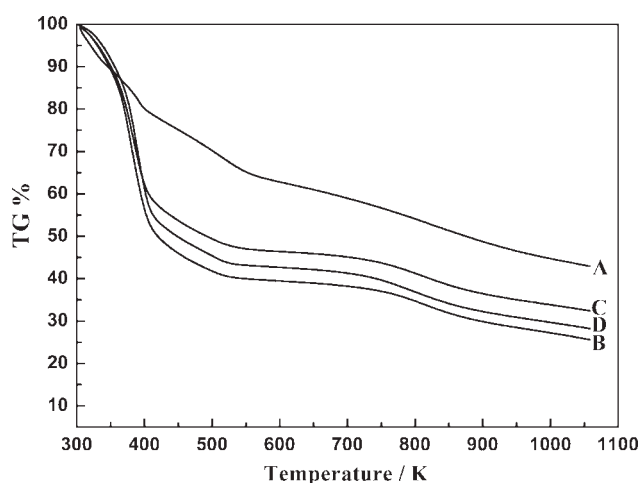


Figure 9 TG curves of (A) poly(*o*DHB-*co*-3MeT) (1 : 1), (B) poly(*o*DHB-*co*-3MeT) (1 : 10), (C) poly(*o*DHB-*co*-3MeT) (1 : 20), and (D) poly(*o*DHB-*co*-3MeT) (1 : 50).

TABLE III
Electrical Conductivities of PoDHB, PMeT, and the Copolymers Prepared in Pure BFEE at Constant Applied Potentials of 1.1, 1.2, and 1.2 V

Sample	Conductivity (S/cm)
PoDHB	0.064
Poly(<i>o</i> DHB- <i>co</i> -3MeT) (1 : 1)	0.2
Poly(<i>o</i> DHB- <i>co</i> -3MeT) (1 : 10)	1.25
Poly(<i>o</i> DHB- <i>co</i> -3MeT) (1 : 20)	2.27
Poly(<i>o</i> DHB- <i>co</i> -3MeT) (1 : 50)	4.8
PMeT	63.2

copolymer as the temperature increased. All of the aforementioned results indicated good thermal stability in the copolymers.

Electrical conductivity

The electrical conductivities of PoDHB, PMeT, and their copolymers obtained potentiostatically from BFEE at constant applied potentials of 1.1, 1.2, and 1.2 V, respectively, were investigated. PMeT exhibited excellent electrical conductivity in this study, up to 63.2 S/cm, whereas the electrical conductivity of PoDHB was about 6.4×10^{-2} S/cm. The electrical conductivities of the copolymers were between those of PMeT and PoDHB, as shown in Table III. This indicated that the insertion of 3MeT units into PoDHB was greatly helpful for the enhancement of the electrical conductivity of PoDHB, which may be beneficial for the extension of the applications of PoDHB.

The film quality of the PMeT was quite good; the film could be peeled off the electrode into a free-standing state. The films were easily cut into various shapes with a knife. On the other hand, the film quality of PoDHB was not quite that good. After the copolymerization of *o*DHB and 3MeT, the copolymer films could also be peeled from the electrode surface as free-standing films. These properties may also be very helpful for their applications.

CONCLUSIONS

The electrochemical copolymerization of *o*DHB and 3MeT was successfully realized in BFEE by direct anodic oxidation of *o*DHB and 3MeT monomer mixtures. The properties of the as-formed poly (*o*DHB-*co*-3MeT) films depended on the feed ratios of the monomer mixtures. The incorporation of 3MeT into the PoDHB chain overcame the low conductivity derived from the poor quality of the PoDHB film. Under these conditions, the as-formed copolymer films showed the advantages, such as good redox activity, electrical conductivity, and thermal stability, of both PoDHB and PMeT. Fluorescence studies

revealed that the copolymer was a good blue–yellow-light emitter with two emission peaks at 383 and 523 nm. In addition, the emission intensity of the copolymer was easily tuned by manipulation of the monomer feed ratio.

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