

# Electrochemical copolymerization of 9,10-dihydrophenanthrene and 3-methylthiophene and characterization of their copolymer with tunable fluorescence properties

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**Abstract** Electrochemical copolymerization of 9,10-dihydrophenanthrene and 3-methylthiophene was successfully achieved in boron trifluoride diethyl etherate by direct anodic oxidation of the monomer mixtures. The structure and properties of the copolymers were investigated with ultraviolet–visible, Fourier transform infrared spectroscopy,  $^1\text{H}$  nuclear magnetic resonance, fluorescence spectra, and thermal analysis. The novel copolymers had the advantages of both poly(9,10-dihydrophenanthrene) and poly(3-methylthiophene), such as good electrochemical behavior, good mechanical properties, and high electrical conductivity. Fluorescence spectroscopy studies revealed that the copolymers had good fluorescence properties, and the emitting properties of the copolymer could be parameters by changing the feed ratio of the monomer mixtures during the electrochemical polymerization.

**Keywords** Electrochemical copolymerization · Conducting polymers · Poly(3-methylthiophene) · Poly(9,10-dihydrophenanthrene)

## Introduction

The synthesis of novel conducting polymer films has been an increasingly important subject of intensive research [1–3], owing to the fact that these films possess desirable physical, chemical, and electrochemical properties for use in many applications, such as biosensors, microsized

reversible conductive polymer electrodes, rechargeable batteries, actuators, and optoelectronics [4–10]. Among these polymers, polyphenanthrene and its derivatives have unique optical and nonlinear optical properties and have potential applications in the fabrication of sensors, rechargeable batteries, and electroluminescence devices [11–13]. As a novel conducting polymer, poly(9,10-dihydrophenanthrene) (PDHP) has been successfully electrosynthesized by direct anodic oxidation of its monomer 9,10-dihydrophenanthrene (DHP) in boron trifluoride diethyl etherate (BFEE), with good fluorescence property as blue light-emitting materials together with good thermal stability [14]. However, it also has disadvantages, such as the poor mechanical properties, and the low electrical conductivity which limits its application. It is well known that copolymerization is one of efficient approaches to modify the properties of conducting polymers, which can produce copolymers with properties being intermediate between individual polymers. By means of the electrochemical copolymerization, some new conducting polymers have been prepared with several obvious advantages, such as variation of electrical conductivity, enhancement of electrochemical activity, and improvement of thermal stability. Poly(3-methylthiophene) (PMeT), an important derivative of polythiophene, has also been the subject of intense research because of its high electrical conductivity (close to  $750\text{ S cm}^{-1}$  [15]), high tensile strength, and good flexibility [16]. High-quality freestanding films of PMeT can be easily produced by direct anodic oxidation of 3MeT monomer in BFEE [17]. Until now, PMeT-based copolymers have been prepared successfully by direct electrochemical oxidation of the mixtures of 3MeT with other corresponding monomers [18–26]. PDHP is a good blue-light emitter. On the other hand, PMeT has the advantage of

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easy electrodeposition of freestanding films with high electrical conductivity. If DHP and 3MeT were copolymerized successfully, this novel copolymer with properties intermediate between their properties may meet the application of PDHP in polymer light-emitting diodes (PLEDs) as light-emitting thin films. So, it would be significant to copolymerize DHP with 3MeT, and this is also a challenge at the same time.

In this article, DHP and 3MeT were copolymerized successfully by direct electrochemical oxidation of the monomer mixtures in BFEE. The electrochemistry of PDHP, PMeT, and copolymers were studied. In addition, the spectroscopic properties, electrical conductivity, and thermal stability of the copolymer were also investigated in detail.

## Experimental

### Materials

BFEE (Beijing Changyang Chemical Plant) was distilled and stored at  $-20\text{ }^{\circ}\text{C}$  before use. DHP (96%; Tokyo Chemical Industry Co., Ltd) and 3MeT (99%; Acros Organics, Fair Lawn, New Jersey) were used directly. Acetone (analytical grade) and dimethyl sulfoxide (DMSO, analytical grade) were products of Tianjin Boding Chemicals Co., Ltd.

### 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, Oakridge, TN) under computer control. During the electrochemical examinations, 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 large amount of polymer to carry out characterization, stainless steel sheets with surface areas of 10 and 12  $\text{cm}^2$  were used as the working electrode and counter electrode, respectively. The stainless steel electrodes were polished with abrasive paper (1,500 mesh) and then washed with acetone before each examination. The typical electrolytic solution was BFEE with different feed ratios of monomer mixtures. BFEE serves not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte is needed. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during the experiments. All potentials were referred to a saturated calomel electrode (SCE). The

homopolymers and copolymers were synthesized at a constant applied potential of 1.3 V. The amount of polymer deposited on the electrode was controlled by the integrated charge passed through the cell. The polymers were scraped from the stainless steel electrode after electropolymerization then washed with water and acetone to remove the electrolyte and monomer. The polymer was in a doped state (oxidized state). However, this would have negative effect on the oxidation state of the polymers. For spectral analyses, they were dedoped with 25% ammonia for 3 days and then washed repeatedly with pure water. At last, they were dried at  $60\text{ }^{\circ}\text{C}$  in vacuum for 2 days.

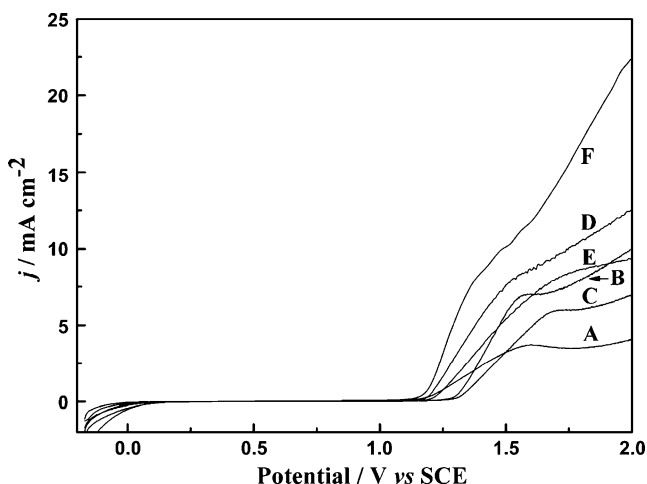
### Characterization

The electrical conductivity of as-formed polymer films was measured by conventional four-probe technique. Ultraviolet–visible (UV–vis) spectra were taken with a PerkinElmer Lambda 900 ultraviolet–visible–near-infrared spectrometer. Infrared spectra were recorded on a Bruker Vertex 70 Fourier transform infrared (FT-IR) with KBr pellets. Mass ratios of KBr and polymer is about 100:1. Fluorescence spectrum was determined with an F-4500 fluorescence spectrophotometer (Hitachi).  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400 NMR spectrometer, and  $\text{CD}_3\text{SOCD}_3$  was used as solvent. Thermogravimetric analysis was performed with a Pyris Diamond TG/DTA (PerkinElmer) thermal analyzer. All thermal analyses were performed under a nitrogen stream in the temperature range of 300–1,100 K at a heating rate of  $10\text{ K min}^{-1}$ .

## Results and discussion

### Electrochemical copolymerization

In order to determine the proper conditions for electrocopolymerization in BFEE system, the anodic oxidation of DHP and 3MeT was first examined. The onset oxidation potential ( $E_{\text{ox}}$ ) of DHP polymerization was 1.13 V (Fig. 1 a), and that for 3MeT was 1.18 V (Fig. 1 f). On the basis of the traditional view of electrocopolymerization, the success of copolymerization is mainly because of the closeness of the oxidation potentials of two monomers. The small distinction (0.05 V) between  $E_{\text{ox}}$  of the two monomers implied the possibility of their electrochemical copolymerization, which would extend the applications of both PDHP and PMeT. To identify proper stoichiometries for copolymer formation, various feed ratios of DHP and 3MeT were tested. When the feed ratio of DHP to 3MeT was 2:1,  $E_{\text{ox}}$  of the copolymer was 1.26 V (Fig. 1 b). When the feed ratios of DHP to 3MeT were 1:1, 2:3, and 1:2, the  $E_{\text{ox}}$  of the



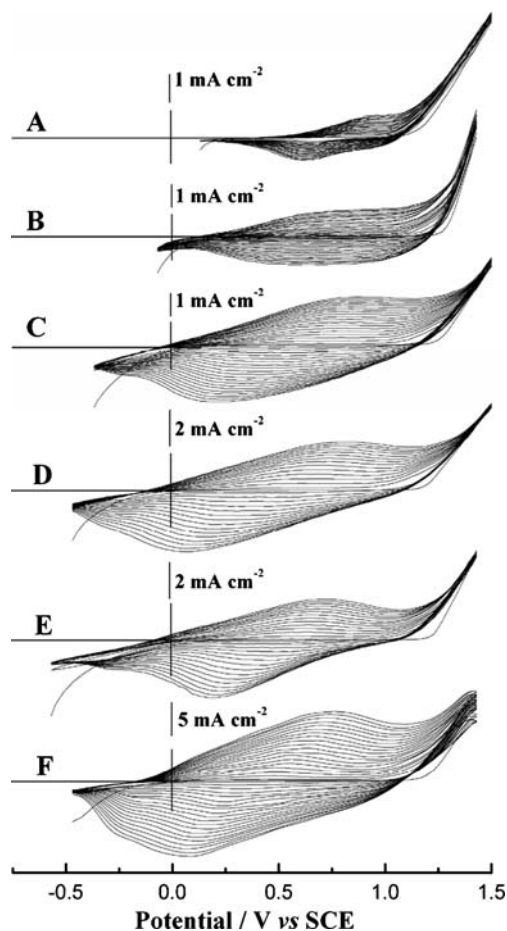
**Fig. 1** Anodic polarization curves of 0.02 mol L<sup>-1</sup> DHP (a), 0.02 mol L<sup>-1</sup> DHP and 0.01 mol L<sup>-1</sup> 3MeT (b), 0.02 mol L<sup>-1</sup> DHP and 0.02 mol L<sup>-1</sup> 3MeT (c), 0.02 mol L<sup>-1</sup> DHP and 0.03 mol L<sup>-1</sup> 3MeT (d), 0.02 mol L<sup>-1</sup> DHP and 0.04 mol L<sup>-1</sup> 3MeT (e), and 0.05 mol L<sup>-1</sup> 3MeT (f) in BFEE. The potential scan rate was 20 mV s<sup>-1</sup>

copolymer were 1.29, 1.15, and 1.19 V, respectively (Fig. 1 c–e). As can be seen from Fig. 1,  $E_{ox}$  of the copolymers different from  $E_{ox}$  of DHP and 3MeT, this suggested that the two monomers maybe oxidized together, and the copolymer chains were composed of both DHP and 3MeT units.

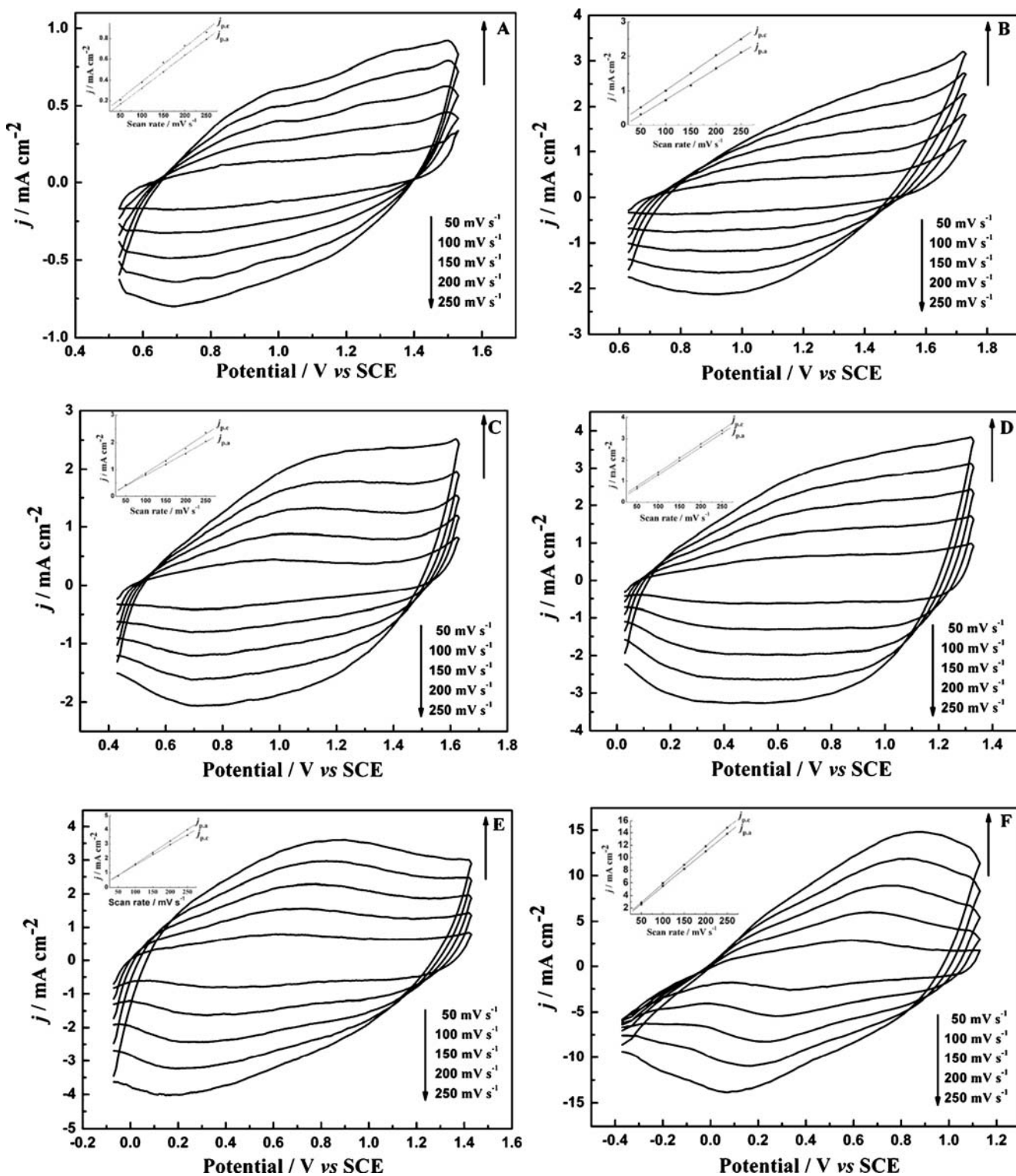
The successive cyclic voltammograms (CVs) of DHP, 3MeT, and mixtures of the two monomers with various feed ratios in BFEE at a potential scanning rate of 100 mV s<sup>-1</sup> are illustrated in Fig. 2. It can be clearly seen from Fig. 2 that as the potential scanning continued, PDHP films were formed on the working electrode surface. The increase in the redox wave currents implied that the amount of the polymer on the electrode was increasing. The potential shift of the wave current maximum provided the information about the augmentation of the electrical resistance in polymer film and the overpotential required to overcome the resistance [27]. PDHP could be reduced and oxidized between 0.61 and 0.92 V (Fig. 2 a). On the other hand, CVs of PMeT showed broad redox waves with reduction and oxidation peaks at 0.08 and 0.76 V, respectively (Fig. 2 f). With the increasing in the 3MeT concentration, great changes can be easily observed in CVs (Fig. 2 b–e). When the concentration of 3MeT was increased to 0.04 mol L<sup>-1</sup>, the CVs curve of the copolymer was very similar to that of PMeT, implying that more 3MeT units were incorporated into the copolymer film (Fig. 2 e). In sharp contrast to homopolymers, the oxidation potential of the copolymer 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 those of homopolymers suggested the formation of copolymers [28].

## Electrochemistry of the copolymer films

In order to investigate the electrochemical behaviors of polymers, PDHP, PMeT, and the copolymer films with various feed ratios were prepared at the constant applied potential of 1.3 V for 50 s, and these polymer films were characterized by CVs in monomer-free BFEE solution, as shown in Fig. 3. In BFEE, with the scanning rates of 50 mV s<sup>-1</sup>, PDHP can be oxidized and reduced from 1.4 (anodic peak potential) to 0.67 V (cathode peak potential; Fig. 3a), and PMeT can be oxidized and reduced from 0.61 to 0.34 V (Fig. 3f). The copolymer films prepared from feed ratios of DHP/3MeT were 2:1 and 1:1 can be oxidized and reduced from 1.45 to 0.84 V and from 0.98 to 0.70 V (Fig. 3b, c). When the feed ratios of DHP/3MeT were 2:3 and 1:2, the copolymers can be oxidized and reduced from 0.87 to 0.44 V and from 1.42 to 0.97 V (Fig. 3d, e). The peak current densities were proportional to potential scan rates (inset of Fig. 3), indicating a redox couple fixing on



**Fig. 2** CVs of 0.02 mol L<sup>-1</sup> DHP (a), 0.02 mol L<sup>-1</sup> DHP and 0.01 mol L<sup>-1</sup> 3MeT (b), 0.02 mol L<sup>-1</sup> DHP and 0.02 mol L<sup>-1</sup> 3MeT (c), 0.02 mol L<sup>-1</sup> DHP and 0.03 mol L<sup>-1</sup> 3MeT (d), 0.02 mol L<sup>-1</sup> DHP and 0.04 mol L<sup>-1</sup> 3MeT (e), and 0.05 mol L<sup>-1</sup> 3MeT (f) in BFEE. The potential scan rate was 100 mV s<sup>-1</sup>



**Fig. 3** CVs of **a** PDHP, **b** poly(DHP-co-3MeT=2:1), **c** poly(DHP-co-3MeT=1:1), **d** poly(DHP-co-3MeT=2:3), **e** poly(DHP-co-3MeT=1:2), and **f** PMeT recorded in monomer-free BFEE. The potential

scan rates were 50, 100, 150, 200, and 250  $\text{mV s}^{-1}$ .  $j_{p,a}$ ,  $j_{p,c}$  are defined as the anodic peak current densities, and the cathodic peak current densities, respectively

the electrode [29]. The polymer films can be cycled repeatedly between the conducting (oxidized) and the insulating (neutral) states without significant decomposition of the materials in BFEE, implying good stability of the polymer.

#### Structural characterization

During the potentiostatic process, the originally colorless solutions 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 with the elongation of the polymer main chain. However, there were still some oligomers, which diffused from the electrode into the bulk solution.

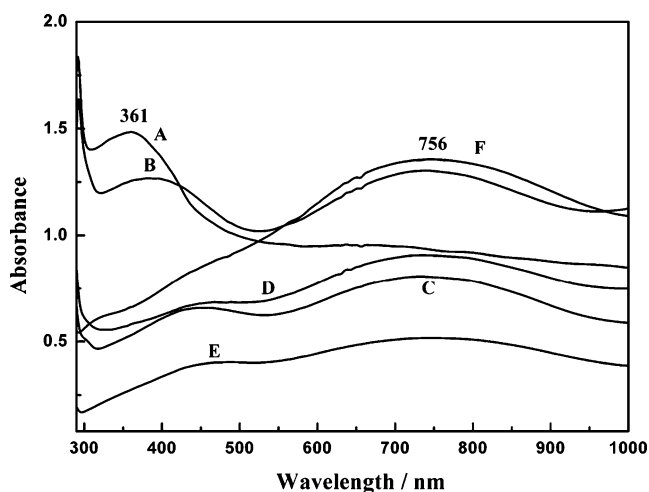
PDHP was black in the doped state. When dedoped, its color was brown. PDHP was partly soluble in organic solvent such as DMSO [14]. PMeT film changed its color from navy blue (doped state) to transparent red (dedoped state) and was almost insoluble in any organic solvents [22]. For the copolymers, their color varied from black (doped state) to red-brown color (dedoped state). The copolymers could partly dissolve in organic solvents such as DMSO.

UV–vis spectra of PDHP, PMeT, and copolymer films deposited on indium–tin–oxide (ITO) electrode at the constant applied potential of 1.3 V for 100 s are shown in Fig. 4. The thickness of the polymer film on ITO glass was controlled by the passage of the same integrated charge into the same area of the ITO surface. Doped PDHP film showed a strong absorption at 361 nm, and the overall absorption tailed off to about 560 nm (Fig. 4 a). A longer wavelength in spectra usually indicates longer polymer

sequences [30]. Doped PMeT film showed a much broader absorption at 650 to 860 nm with a peak at 756 nm (Fig. 4 f), characteristic of the existence of charge carriers in the doped state such as polarons and bipolarons. In the course of the doping process, the originally filled valence band of the PMeT became partially empty. The Fermi level lowered to the valence band, which ensured a metallic behavior of PMeT. It could be expected that the more doped PMeT is, the more empty the valence band would become; as a consequence charge carriers concentration would increase, and hence the electrical conductivity would also increase [16]. Similarly to PDHP and PMeT, the spectra of the copolymers showed characteristic absorptions for both PDHP and PMeT (Fig. 4 b–e). However, there were slight red shifts of the absorption of the copolymer films in comparison with that of PDHP due to incorporation of 3MeT units, further confirming the occurrence of copolymerization.

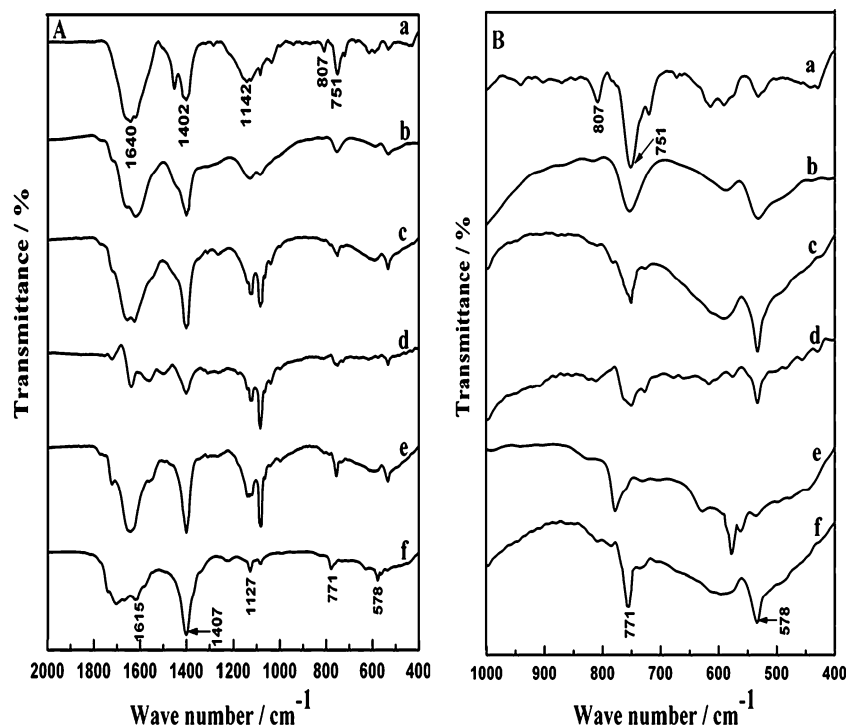
FT-IR spectra of PDHP, PMeT and copolymers, are shown in Fig. 5. In the spectrum of PDHP (Fig. 5a (a)), the bands at 1,402 and 1,640  $\text{cm}^{-1}$  showed the vibrations of the backbone of benzene which could be found for the copolymer. The bands in the region from 1,400 to 1,000  $\text{cm}^{-1}$  were assigned to the stretching and shrinking modes of C=C and C–C. The two peaks at 751 and 815  $\text{cm}^{-1}$ , which were assigned to the three adjacent C–H deformation vibration of ring hydrogens, suggested that the benzene ring of PDHP unit was 1,2,4-trisubstituted which could be also found for the copolymer. This verified that the main component in PDHP had the characteristics of typical conjugated polymers and implied that the electropolymerization of DHP maybe occurred at C<sub>2</sub>-, C<sub>7</sub>- and C<sub>3</sub>-, C<sub>6</sub>- positions. Additional, according to the literature [14], the results of quantitative calculation showed that the electropolymerization of DHP mainly occurred at C<sub>2</sub>-, C<sub>7</sub>- positions.

In the spectrum of PMeT, the bands at 1,615 and 1,127  $\text{cm}^{-1}$ , originated from the stretching modes of C=C on the thiophene ring [31], and the band at 771  $\text{cm}^{-1}$  was assigned to the out-of-plane C–H band, which could be found for the copolymer. As shown in Fig. 5a (f), the characteristic bands of 2,5-disubstituted 3MeT unit clearly appear: the band located at about 1,407  $\text{cm}^{-1}$  was assigned to the deformation of the methyl group [32, 33], and the narrow peak at 578  $\text{cm}^{-1}$  of the PMeT spectrum was the characteristic absorption of the C–S bond which can be also found in copolymers shifted to lower wave numbers. All these characteristic bands of PMeT and PDHP could be found in the spectra of copolymers (Fig. 5a (b–e)), implying that the copolymerization happened during the potentiostatic electropolymerization of DHP and 3MeT and indicated that the coupling reaction mainly occurred at C<sub>2</sub>-, C<sub>5</sub>- position of 3MeT and C<sub>2</sub>-, C<sub>7</sub>- position of DHP (Scheme 1) in well accordance with the literature [14, 16].



**Fig. 4** UV–visible spectra of PDHP (a), poly(DHP-co-3MeT=2:1) (b), poly(DHP-co-3MeT=1:1) (c), poly(DHP-co-3MeT=2:3) (d), poly(DHP-co-3MeT=1:2) (e), and PMeT (f)

**Fig. 5** **a** Infrared spectra of PDHP (a), poly(DHP-co-3MeT=2:1) (b), poly(DHP-co-3MeT=1:1) (c), poly(DHP-co-3MeT=2:3) (d), poly(DHP-co-3MeT=1:2) (e), and PMeT (f). **b** Zoomed infrared spectra between 1,000 and 400  $\text{cm}^{-1}$



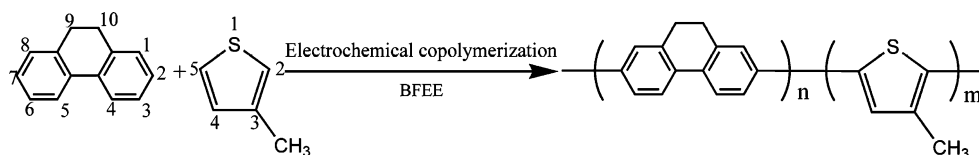
To further investigate copolymer structure,  $^1\text{H}$  NMR spectra of DHP, 3MeT, and copolymer were recorded. As shown in Fig. 6 a, the spectrum of DHP showed two groups of protons: the proton chemical shift from ca. 7.78 to 7.85 can be ascribed to the proton at C(4) and C(5), and that from ca. 7.20 to 7.36 can be ascribed to the proton at C(1), C(2), C(3), C(6), C(7), and C(8). According to the spectrum of 3MeT (Fig. 6 c), there were three groups of protons: the proton chemical shift from ca. 7.41 to 7.43 can be ascribed to the proton at C(5), the proton chemical shift from ca. 7.10 to 7.12, and from ca. 6.94 to 6.95 can be ascribed to the proton at C(2) and C(4). The proton lines of copolymer (Fig. 6 b) were broader than the corresponding proton lines of DHP and 3MeT monomer due to the wide molar mass distribution of copolymer. It can be seen that some new peaks appeared after copolymerization, and most of the peaks moved to lower field, which was mainly due to the introduction of higher conjugation length in the copolymer main chain. As illustrated in Fig. 6 b, there were four groups of protons in the copolymer spectra. The proton chemical shift from ca. 7.84 to 7.86 can be ascribed to the proton at C(4) arose from thiophene ring, and the other

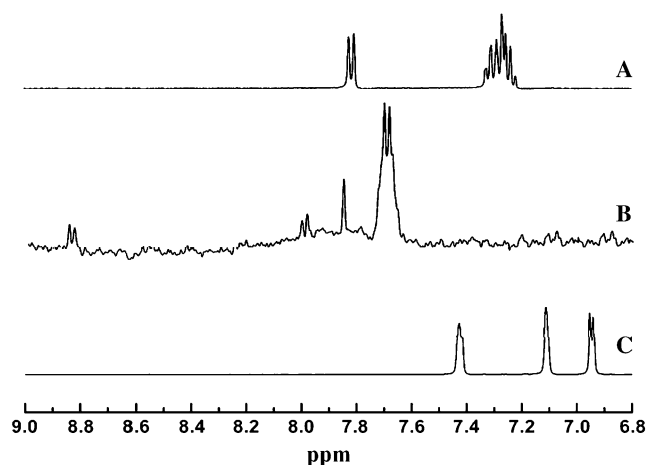
three groups: the proton chemical shift from ca. 7.96 to 8.01, from ca. 8.80 to 8.86, and from ca. 7.63 to 7.76 can be ascribed to the proton at C(6), C(3), and C(1), C(4), C(5), and C(8) arose from the benzene ring of DHP units. Based on these considerations together with the previous reports, the chemical structure of the copolymers can be speculated as in Scheme 1, in well accordance with FT-IR results.

#### Fluorescence properties

The fluorescence spectra of doped and dedoped PDHP and copolymers prepared in BFEE were examined using DMSO as the solvent through the wavelength scans of emission. The emission peak of doped and dedoped PMeT film is close to zero as shown in Fig. 7a (f), b (f). The emission maximum of doped PDHP was mainly at 484 nm with two shoulders at 468 and 499 nm, when excited at 308 nm (Fig. 7a (a)). For the dedoped PDHP, the emission maximum was mainly at 484 nm with one shoulder at 470 nm, and another emission peak at 395 nm, when excited at 308 nm (Fig. 7b (a)). The fluorescence spectra of

**Scheme 1** Proposed chemical structure of the copolymers from DHP and 3MeT





**Fig. 6**  $^1\text{H}$  NMR spectra of DHP (a), 3MeT (c), and copolymer (b) prepared from BFEE containing  $0.02 \text{ mol L}^{-1}$  DHP and  $0.03 \text{ mol L}^{-1}$  3MeT at 1.3 V vs SCE. Solvent:  $\text{CD}_3\text{SOCD}_3$

the doped copolymers prepared from different feed ratios all showed three emission peaks at 368, 390, and 486 nm when excited at 295 nm (Fig. 7a (b–e)). For the dedoped copolymers, the emission maximum was mainly at 484 nm and another two emission peaks at 370 and 390 nm, when excited at 295 nm (Fig. 7b (b–e)). After incorporation of 3MeT units into PDHP chains, upon irradiation with 365 nm UV light, the solutions of copolymers showed different color. When the feed ratio of DHP to 3MeT was 2:1 and 1:1, the color of the solution turned to yellow green in comparison with that of PDHP. When the feed ratio of DHP to 3MeT was 2:3 and 1:2, the color of the solution turned to blue green as shown in Fig. 8.

The fluorescence quantum yields ( $\phi_{\text{overall}}$ ) of the PDHP and copolymer samples were measured by using anthracene in acetonitrile (standard,  $\phi_{\text{ref}}=0.27$ ) as a reference and calculated according to the well-known method based on the expression:

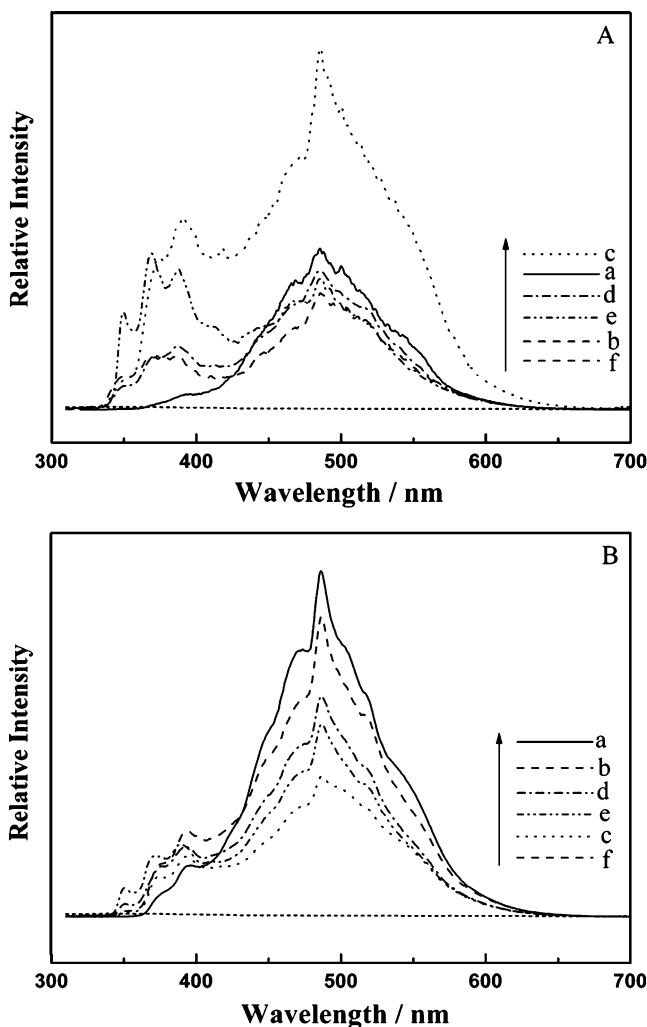
$$\phi_{\text{overall}} = \frac{n^2 A_{\text{ref}} I}{n_{\text{ref}}^2 A I_{\text{ref}}} \phi_{\text{ref}}$$

Here,  $n$ ,  $A$ , and  $I$  denote the refractive index of the solvent, the absorbance at the excitation wavelength, and the intensity of the emission spectrum, respectively. Absorbance of the samples and the standard should be similar [34]. The fluorescence quantum yields of doped PDHP in DMSO were determined to be 0.28. Furthermore, the copolymers also had high fluorescence quantum yields. When the feed ratios of DHP to 3MeT were 2:1, 1:1, 2:3, and 1:2, the fluorescence quantum yields of copolymers were 0.11, 0.17, 0.19, and 0.24. On the basis of these results, the fluorescence properties of copolymers could be easily controlled by changes in the feed ratio of the

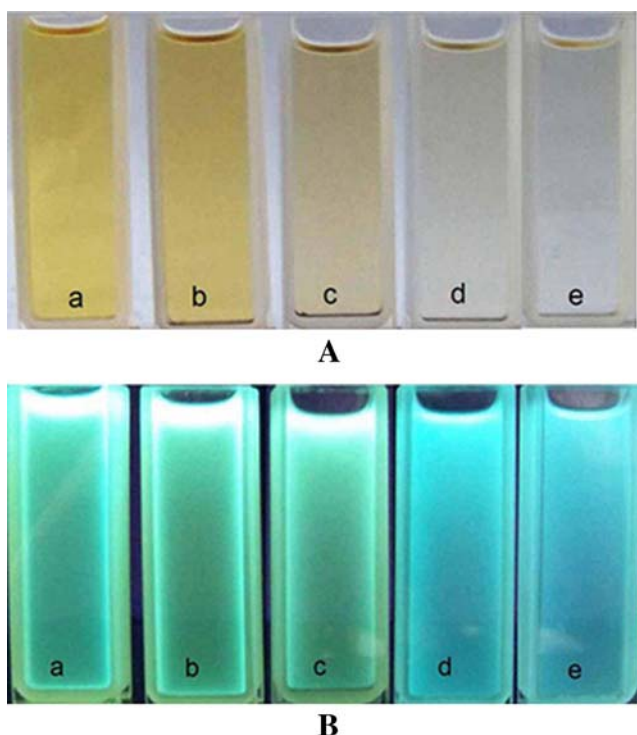
monomer mixtures, and the copolymers are good light-emitting materials.

#### Thermal analysis

The degradation behavior of conducting polymers is very important for their potential applications. PDHP and PMeT both have good thermal stability [14, 16]. Therefore, the thermal analyses of copolymers were tested by thermogravimetric analysis as shown in Fig. 9. All thermal analyses were performed under a nitrogen stream in the temperature range of 300–1,100 K with a heating rate of  $10 \text{ K min}^{-1}$ . For poly (DHP/3MeT=1:1), the first decomposition started

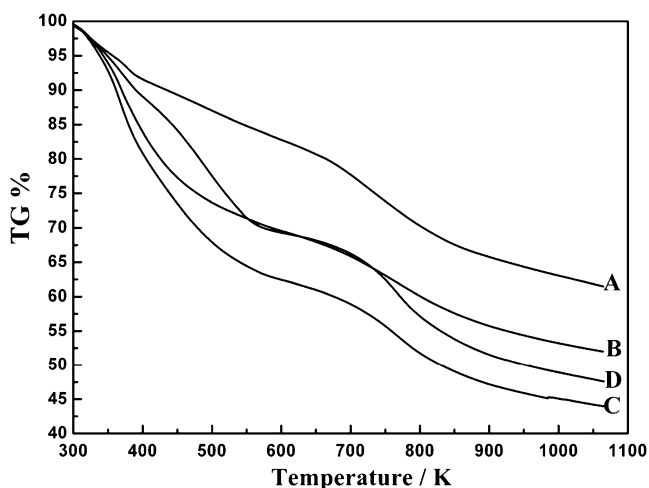


**Fig. 7** a Fluorescence spectra of doped PDHP (a), doped poly(DHP-co-3MeT=2:1) (b), doped poly(DHP-co-3MeT=1:1) (c), doped poly(DHP-co-3MeT=2:3) (d), doped poly(DHP-co-3MeT=1:2) (e), and doped PMeT (f). Solvent: DMSO. b Fluorescence spectra of dedoped PDHP (a), dedoped poly(DHP-co-3MeT=2:1) (b), dedoped poly(DHP-co-3MeT=1:1) (c), dedoped poly(DHP-co-3MeT=2:3) (d), dedoped poly(DHP-co-3MeT=1:2) (e), and dedoped PMeT (f). Solvent: DMSO



**Fig. 8** **a** Photographs of PDHP (a), poly(DHP-co-3MeT=2:1) (b), poly(DHP-co-3MeT=1:1) (c), poly(DHP-co-3MeT=2:3) (d), and poly(DHP-co-3MeT=1:2) (e), dissolving in DMSO. **b** Photographs of PDHP (a), poly(DHP-co-3MeT=2:1) (b), poly(DHP-co-3MeT=1:1) (c), poly(DHP-co-3MeT=2:3) (d), and poly(DHP-co-3MeT=1:2) (e), dissolving in DMSO under UV irradiation (365 nm)

to lose weight at about 300 to 650 K, which can be ascribed to moisture evaporation in the polymer and the decomposition of the doping species [35, 36]. The second decomposition of the copolymer started from 650 to 830 K, this weight loss was attributed to the degradation



**Fig. 9** Thermogravimetric curves of poly(DHP-co-3MeT=2:1) (a), poly(DHP-co-3MeT=1:1) (b), poly(DHP-co-3MeT=2:3) (c), and poly(DHP-co-3MeT=1:2) (d)

of the skeletal copolymer main backbone. Other small decomposition occurred between 830 and 1,060 K, possibly because of the overflow of some oligomers that decomposed from the copolymer with the temperature increasing. Similar results can also be observed from other copolymers with different feed ratios, indicating good thermal stability of copolymers.

#### Electrical conductivity

The electrical conductivities of PDHP, PMeT, and their copolymers obtained potentiostatically from BFEE were investigated. The electrical conductivity of PDHP was about  $4.2 \times 10^{-2} \text{ S cm}^{-1}$ , whereas PMeT exhibited higher electrical conductivity, up to  $58.7 \text{ S cm}^{-1}$ . The electrical conductivities of the copolymers were between those of PDHP and PMeT, as shown in Table 1. This indicated that the insertion of 3MeT units into PDHP was greatly helpful for the enhancement of the electrical conductivity of PDHP, which may be beneficial for the extension of the applications of PDHP.

The film quality of PMeT prepared from BFEE was quite good, which can be peeled off the electrode into freestanding state. On the other hand, the PDHP films prepared from BFEE are brittle. After copolymerization of DHP and 3MeT, the copolymer films can also be peeled from the electrode surface as freestanding films. Compared to PDHP films, the mechanical properties of copolymers have been improved. These properties may also be very helpful for their applications.

#### Conclusion

The electrochemical copolymerization of DHP and 3MeT was successfully realized in BFEE by direct anodic oxidation of DHP and 3MeT monomer mixtures. The properties of as-formed poly(DHP-co-3MeT) films depended on the feed ratios of the monomer mixtures. The incorporation of 3MeT into the PDHP chain overcame the low conductivity and the poor mechanical properties of

**Table 1** Electrical conductivities of PDHP, P3MeT, and copolymers prepared in BFEE at the constant applied potential of 1.3 V

Sample	Conductivity ( $\text{Scm}^{-1}$ )
Poly(DHP)	0.04
Poly(DHP/3MeT=2:1)	0.12
Poly(DHP/3MeT=1:1)	0.89
Poly(DHP/3MeT=2:3)	1.58
Poly(DHP/3MeT=1:2)	3.26
Poly(MeT)	58.7



the PDHP film. The copolymers showed many advantages, such as good electrochemical behavior, high electrical conductivity, good mechanical properties, and favorable thermal stability. Fluorescence studies revealed that the copolymer was good blue green-light emitter. In addition, the emission intensity of the copolymer could be easily tuned by the monomer feed ratios. Under these conditions, as-formed copolymer films combined with the advantages of both PDHP and PMeT may meet the application in PLEDs as light-emitting thin films.

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