

# Electrochemical Copolymerization of 3,4-Ethylenedioxythiophene and 5-Methylindole and Characterizations of the Copolymers

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**ABSTRACT:** Electrocopolymerization of 3,4-ethylenedioxythiophene (EDOT) and 5-methylindole (5MeIn) was successfully carried out in acetonitrile containing lithium perchlorate as supporting electrolyte although the oxidation potentials of 5MeIn and EDOT were quite different. The influence of feed ratios and applied potentials on the copolymerization were investigated. The novel low band gap copolymers own both the advantages of P5MeIn and poly(3,4-ethylenedioxythiophene), i.e., good redox activity, good thermal stability, and high

conductivity. The resulting copolymers were characterized by electrochemistry, FT-IR and ultra violet-visible spectroscopy, elemental analysis, thermal analysis, conductivity, and scanning electron microscopy, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 373–381, 2008

**Key words:** inherently conducting polymers; electrochemical copolymerization; poly(3,4-ethylenedioxythiophene); polyindole; copolymer

## INTRODUCTION

Inherently conducting polymers (ICPs) are of particular interest due to their potential industrial applications in some fields based on their  $\pi$ -conjugated electronic structures, high conductivity, and good environmental stability. Among ICPs, poly(3,4-ethylenedioxythiophene) (PEDOT), an important polythiophene derivative with two electron-donating oxygen atoms of the 3,4-positions of thiophene, has become one of the most popular conducting polymers being studied by many scientific research groups.<sup>1,2</sup> PEDOT shows better properties, such as high conductivity, environmental stability, relatively low bandgap, good chemical and electrochemical properties when compared to unsubstituted polythiophene.<sup>3,4</sup> On the other hand, polyindole (PIIn) has also been received considerable attention as an interesting ICP<sup>5,6</sup> for its several advantages, especially fairly good thermal stability due to the incorporation of benzene rings on the polymer backbone<sup>7</sup> and high

redox activity and stability.<sup>8</sup> However, like other polythiophene derivatives, PEDOT begins to decompose at relatively low temperature, which may inhibit its potential applications. It is well known that one of efficient approaches to modify the properties of ICPs is the electrochemical copolymerization, which can produce copolymers with properties being intermediate between individual polymer.<sup>9</sup> Recently, to modify the properties of PEDOT, lots of research works have been focused on the electrochemical copolymerization of ethylenedioxythiophene (EDOT) with pyrrole,<sup>9,10</sup> thiophene,<sup>11</sup> indole,<sup>12</sup> fluorene, and its derivatives.<sup>13,14</sup> In addition, PIIn shows relatively low electrical conductivity, close to  $10^{-1}$  S cm<sup>-1</sup> in doped state,<sup>15</sup> together with poor mechanical property, which may restrict its applications. Similar to the electrocopolymerization of EDOT, copolymers obtained from Indole with different monomers have also been electrochemically synthesized.<sup>12,16,17</sup> By means of the electrochemical copolymerization, some new conducting polymers have been prepared with several obvious advantages, such as variation of conductivity, enhancement of electrochemical activity, and thermal stability. It is well known that the band gap of ICPs is a crucial factor to improve the properties of semiconductors, which is the difference in energy e.g. between the valence band (HOMO) and the conduction band (LUMO).<sup>18</sup> Intrinsic conductors owe their conductivities to the partial filling of the valence band up to the Fermi-level. To imitate such a par-

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tially filled band with a semiconductor, their band gap should be zero or close to zero. Thus, the lower is the band gap, the better may be the electrical conductivities of ICPs. Generally, the electron-donating group (donor) substitution can increase the HOMO level while the electron-withdrawing group (acceptor) substitution can decrease the LUMO level. Thus the high-lying HOMO of the donor fragment and the low-lying LUMO of the acceptor fragment can yield an unusually small HOMO-LUMO separation,<sup>19</sup> which also leads to a smaller band gap. Therefore, there were concentrated investigations on the electron donating group, such as poly(3-methylthiophene)<sup>20</sup> and PEDOT,<sup>4</sup> which indicated that it was easy to prepare high-quality polymer in contrast to thiophene monomer due to the decrease of band gap. Recently, we obtained poly(5-methylindole) (P5MeIn) with high thermal stability by direct anodic oxidation of 5-methylindole (5MeIn), with an electron donating group on the 5-position of indole.<sup>21</sup> Nevertheless, some drawbacks affect dramatically the applications of P5MeIn, such as relatively low conductivity. By means of electrocopolymerization, it may be beneficial to enhance its conductivity by introduction of EDOT units to P5MeIn main chain due to the high conductivity of PEDOT. However, to the best of our knowledge, electrochemical copolymerization of EDOT and 5MeIn has not been reported so far because the oxidation potentials of 5MeIn and EDOT were quite different. Based on these considerations, it would be interesting to copolymerize 5MeIn and EDOT electrochemically so that as-formed copolymers may have both the advantages of high conductivity of PEDOT and good thermal stability of P5MeIn. In this article, 5MeIn and EDOT were copolymerized successfully by electrochemical oxidation of monomer mixtures. The obtained copolymers were characterized by electrochemistry, FT-IR, UV-vis spectra, and element analysis. The thermal stability, conductivity, and morphology of the copolymer were also investigated.

## EXPERIMENTAL

### Materials

EDOT (98%; Aldrich) and 5MeIn (99%; Acros Organics) were used as received without further purification. Lithium perchlorate ( $\text{LiClO}_4$ , Aldrich) was dried in vacuum at 80°C for 24 h before use. Commercial HPLC grade acetonitrile (ACN, made by Shanghai Chemical Reagent Company) was dried and distilled before use.

### Electrochemical experiments

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of

a Model 263 potentiostat-galvanostat (EG and G Princeton Applied Research) under computer control at room temperature. The working and counter electrodes for cyclic voltammetric experiments were platinum wires with a diameter of 0.5 mm placed 0.5 cm apart. They were polished and cleaned by water and acetone successively before each examination. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 and 12 cm<sup>2</sup> each were employed as working and counter electrodes, respectively. Stainless steel electrodes were carefully polished with abrasive paper (1500 mesh), subsequently cleaned by water and acetone successively before each examination. All potentials were referred to a saturated calomel electrode. The polymers were deposited on an indium-tin-oxide coated glass for UV-visible spectral measurements.

All the samples were grown in an ACN solution containing 0.1 mol L<sup>-1</sup>  $\text{LiClO}_4$  as a supporting electrolyte. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during experiments. The amount of polymer deposited on the electrode was controlled by the integrated charge passed through the cell. To remove the electrolyte and oligomers/monomers, the polymer films were rinsed with water and acetone. For spectral analysis, the polymer was dried under vacuum at 60°C for 2 days.

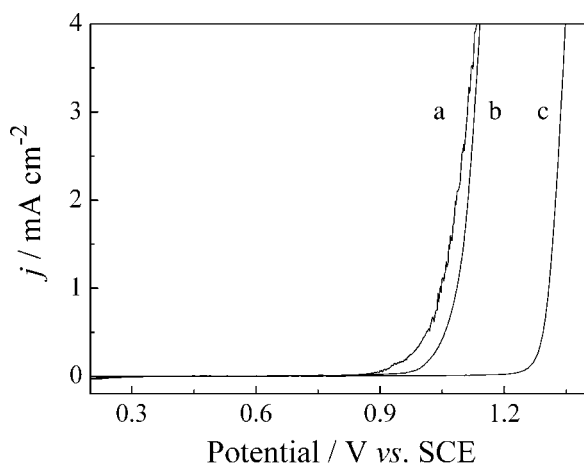
### Characterizations

The conductivity of as-formed polymer films was measured by conventional four-probe technique. UV-visible spectra were taken by using Cary 50 UV-Vis-NIR spectrophotometer. Infrared spectra were recorded using Nicolet 510P FT-IR spectrometer with KBr pellets. Elemental composition of these polymers were determined by Vairo EI III elemental analyzer. Differential scanning calorimetry (DSC) was made with a NETZSCH DSC 204 F1, operating at a heating rate of 5 K min<sup>-1</sup> under N<sub>2</sub> atmosphere. An empty aluminum pan was used as reference. The thermogravimetric analysis (TGA) were performed with a thermal analyzer of NETZSCH TG209. All thermal analysis was performed under a nitrogen stream in the temperature range of 303–1073 K with a heating rate of 10 K min<sup>-1</sup>. Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6700F SEM.

## RESULTS AND DISCUSSION

### Electrochemical copolymerization

To ensure the copolymerization of 5MeIn and EDOT in ACN containing 0.1 mol L<sup>-1</sup>  $\text{LiClO}_4$ , the electro-



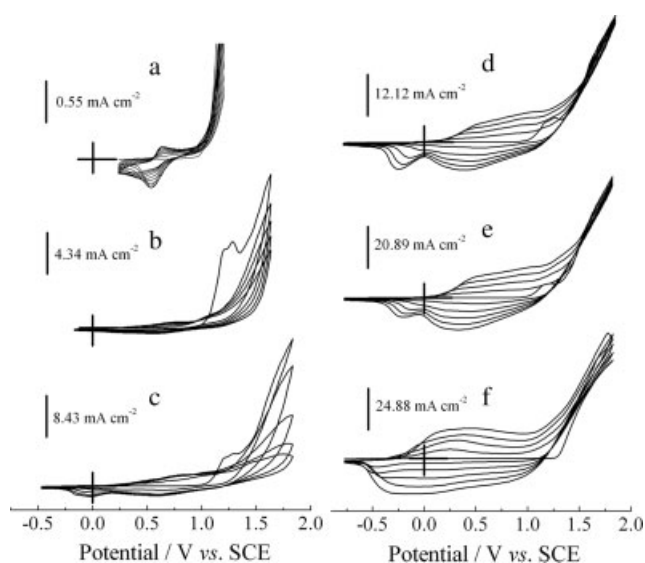
**Figure 1** Anodic polarization curves of (a) 0.02 mol L<sup>-1</sup> 5MeIn, (b) 0.02 mol L<sup>-1</sup> 5MeIn + 0.04 mol L<sup>-1</sup> EDOT and (c) 0.04 mol L<sup>-1</sup> EDOT in ACN/LiClO<sub>4</sub>. Scanning rates: 20 mV s<sup>-1</sup>.

chemical experiments were classified into different groups on the basis of feed ratios of two monomers. The similar results obtained from above different experiments were that the oxidation potential of EDOT was much higher than that of 5MeIn ( $\Delta E = 0.33$  V), where  $\Delta E$  is the difference of the oxidation potentials between EDOT and 5MeIn. It is well known that successful electrochemical copolymerization of different monomers is due to the fact that the oxidation potentials of the monomers are close to each other.<sup>22</sup> From this point, it seems that it is nearly impossible to achieve the electrochemical copolymerization of EDOT and 5MeIn. To realize the copolymerization successfully, we tried to solve this problem by the strategy of diffusion method.<sup>23</sup> Under diffusion limited conditions EDOT oxidation occurred, which implied that the copolymerization was feasible. After a series of experiments with different feed ratios, the concentration of EDOT and 5MeIn was chosen as 0.04 and 0.02 mol L<sup>-1</sup>, respectively.

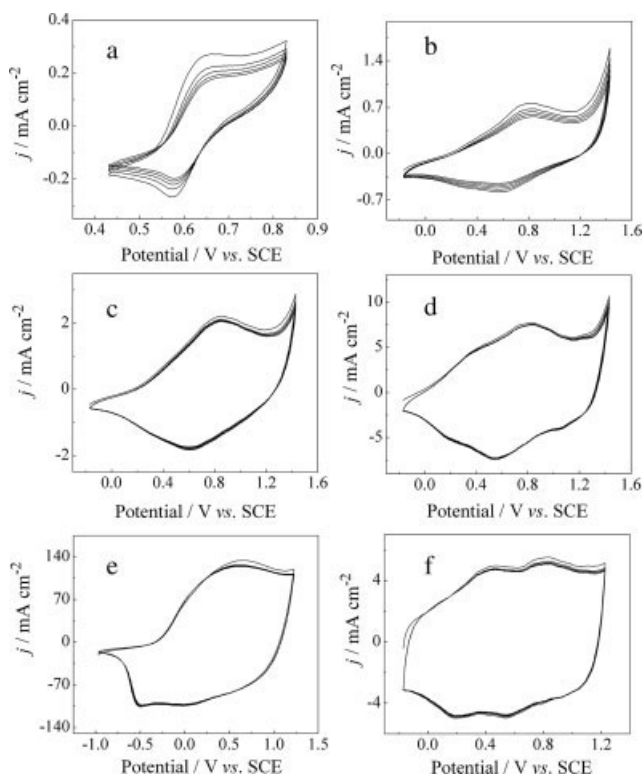
Figure 1 shows the typical anodic polarization curves taken in ACN containing 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> at a potential scanning rate of 20 mV s<sup>-1</sup>. It should be noted here that the background electrolyte is electrochemically silent in the whole potential range. The oxidation onset of 5MeIn was initiated at 0.92 V [Fig. 1(a)] and that of EDOT was 1.25 V [Fig. 1(c)]. When the electrolytic solutions contained 0.04 mol L<sup>-1</sup> EDOT and 0.02 mol L<sup>-1</sup> 5MeIn, the anodic curve B [Fig. 1(b)] was obtained, which was different from curve A and C. It can be seen that the oxidation onset of this mixture was initiated at 1.05 V, which was intervenient between EDOT and 5MeIn. This may be partly due to some changes of the electrochemical environment caused by successive deposi-

tion of two monomers during the anodic polarization,<sup>23</sup> or partly due to the influence of the low electrical conductivity accompanied by the incorporation of indole unit into the copolymer chain. In addition, the fact that the oxidation potential of mixture was between the value of two monomers indicated that two monomers were oxidized alternately and the copolymer chains were composed of alternate EDOT and 5MeIn units, also indicating the occurrence of copolymerization.

The successive cyclic voltammograms (CVs) of 0.04 mol L<sup>-1</sup> EDOT, 0.02 mol L<sup>-1</sup> 5MeIn and the mixture with different feed ratios of two monomers, taken in ACN containing 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> at potential scanning rates of 50 mV s<sup>-1</sup>, were illustrated in Figure 2. As can be seen from this figure, the CVs showed characteristic features as other conducting polymers such as polythiophene and polypyrrole during potentiodynamic syntheses. As the CV scan continued, a polymer film was also formed on the working electrode surface. The increase in the redox wave currents implied that the amount of polymer on the electrode was increasing. It should be noted that the CVs of P5MeIn was weak in comparison with the redox peaks of PEDOT, which also indicated that the electropolymerization of 5MeIn was more difficult than EDOT. P5MeIn can be reduced and oxidized between 0.53 and 0.64 V [Fig. 2(a)]. On the other hand, the CVs of EDOT showed broad redox waves, similar to the literature.<sup>24</sup> PEDOT can be reduced and oxidized between -0.35 V and 0.55 V [Fig. 2(f)]. When the CVs were taken in the electrolytic solutions containing 0.02 mol L<sup>-1</sup>



**Figure 2** Cyclic voltammograms recorded in ACN/LiClO<sub>4</sub> solution containing (a) 5MeIn (0.02 mol L<sup>-1</sup>), 5MeIn : EDOT = (b) 2 : 1, (c) 1 : 1, (d) 1 : 2, (e) 1 : 3, and (f) EDOT (0.04 mol L<sup>-1</sup>), respectively. Scanning rates: 50 mV s<sup>-1</sup>.



**Figure 3** Cyclic voltammograms recorded in monomer free ACN/LiClO<sub>4</sub> of (a) pure P5MeIn, copolymer obtained from different feed ratios of 5MeIn : EDOT = (b) 2 : 1, (c) 1 : 1, (d) 1 : 2, (e) pure PEDOT, and (f) bilayer (P5MeIn-PEDOT). Scanning rates: 100 mV s<sup>-1</sup>.

5MeIn and 0.01 mol L<sup>-1</sup> EDOT, the oxidation and reduction potentials lied at 0.73 V and 0.45 V, respectively, [Fig. 2(b)]. Great differences in the CVs can be easily observed [Fig. 2(c–e)] with the increase of EDOT in this media. In sharp contrast to pure P5MeIn, the oxidation potentials of the mixture shifted positively while the reduction wave moved negatively. On the other hand, the oxidation and reduction potentials of the mixture both shifted positively when compared with pure PEDOT. The evolution of a new couple waves at a potential different from both pure 5MeIn and EDOT suggested the formation of a copolymer.<sup>10</sup> In addition, as can be seen

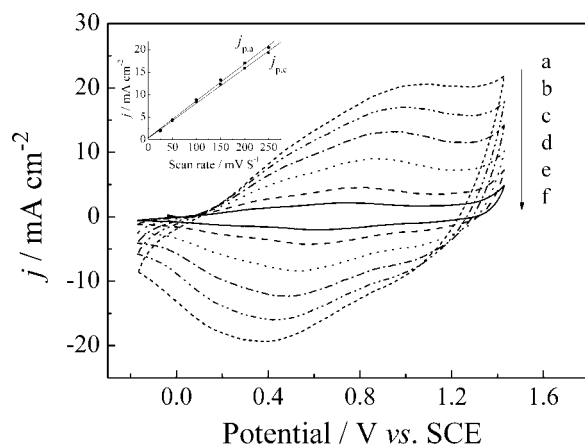
from Figure 2, there was drastic change of the current density between consecutive cycles in comparison with pure 5MeIn and EDOT, which can also be interpreted as the formation of copolymer. It is noteworthy that the color of ACN containing pure 5MeIn darkens during the successive scanning process, indicating soluble indole oligomers formed. However, the quality of copolymer film coated on Pt electrode was higher than pure P5MeIn because copolymer film cannot be dissolved during electrochemical copolymerization, which can be ascribable to the incorporation of EDOT units.

### Electrochemistry of copolymer films

The films of P5MeIn, PEDOT and copolymers of 5MeIn and EDOT with different feed ratios were electrodeposited potentiostatically at 1.1 V after the same polymerization time. The CVs of P5MeIn, PEDOT, and copolymers with different EDOT monomer concentrations from 0.01 mol L<sup>-1</sup> to 0.04 mol L<sup>-1</sup> were given in Figure 3, respectively. In each case, five CV were recorded to ensure reproducibility. The redox wave values of the copolymers obtained from different feed ratios were listed in Table I. It can be seen from Table I that the anodic potential of copolymer shifted positively while the cathodic potential moved negatively with the increase of EDOT concentration, which was in accordance with the results of successive CV (Fig. 2). For example, when the feed ratio was 0.02:0.01, the copolymer showed a couple of redox waves at 0.83 V and 0.59 V, which was similar to P5MeIn. When the feed ratio became 0.02:0.04, the redox profile was close to PEDOT. As shown in Figure 3(a), the redox current densities decreased rapidly cycle by cycle during CVs, which implied that the stability of P5MeIn films was not very good. In sharp contrast to P5MeIn films, the steady-state CV of PEDOT films represented broad and stable anodic and cathodic peaks [Fig. 3(e)], which could be cycled repeatedly without obvious decomposition, indicating the high stability of PEDOT films. Moreover, the decomposition of copolymer was not obvious in contrast to P5MeIn, which can be ascribable to the incorporation

**TABLE I**  
Redox Peak Values of Copolymers Obtained from ACN+0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> Solution Containing 0.02 mol L<sup>-1</sup> 5MeIn and Different Amounts of EDOT

Feed ratio (5MeIn : EDOT)	5MeIn (0.02)	0.02 : 0.01	0.02 : 0.02	0.02 : 0.04	EDOT (0.04)
Polymerization potential (V)	1.2	1.2	1.2	1.2	1.2
Polymerization time (s)	100	100	100	100	100
Anodic potential (V)	0.65	0.83	0.84	0.86	0.61
Cathodic potential (V)	0.61	0.59	0.58	0.55	0.51
Anodic current density (mA cm <sup>-1</sup> )	0.26	0.75	2.18	7.65	131.17
Cathodic current density (mA cm <sup>-1</sup> )	-0.26	-0.58	-1.78	-7.34	-103.32



**Figure 4** Cyclic voltammograms of copolymer in monomer free ACN containing  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  solution at potential scanning rates of (a) 250, (b) 200, (c) 150, (d) 100, (e) 50, (f)  $25 \text{ mV s}^{-1}$ . The copolymer films were prepared from ACN +  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  solution containing  $0.02 \text{ mol L}^{-1} \text{ 5MeIn}$  and  $0.04 \text{ mol L}^{-1} \text{ EDOT}$  at  $1.1 \text{ V}$ .

of EDOT units into the copolymer chain. Therefore, it can be reasonably concluded that the copolymer film shows higher electrochemical stability than P5MeIn. It should be noted here that the CVs of the bilayer (P5MeIn-PEDOT composite), prepared by successive polymerization of PEDOT and P5MeIn, were only the sum of the voltammograms of PEDOT and P5MeIn, as shown in Figure 3(f). It is quite different from those of the copolymers, which further confirms the occurrence of copolymerization.<sup>17</sup>

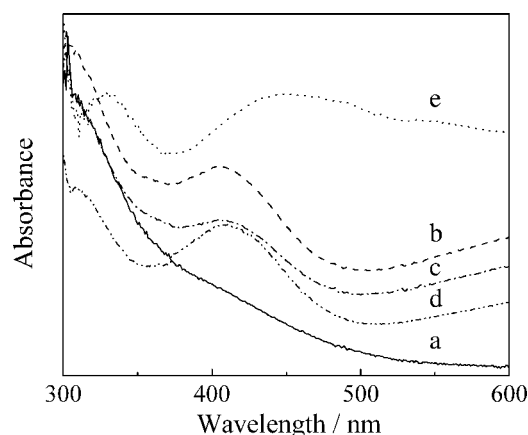
It is well known that PEDOT can be used as stable conducting material in tantalum capacitors owing to its pretty good redox properties.<sup>25</sup> According to Figure 3(e), a rapid increase in current density occurred during the process of potential scan followed by a plateau, while the reverse course showed discharge of stored charge as the capacitor returned to its original state, indicating a distinct capacitive feature of the charge storage. As is shown in Figure 3, the electrochemical activity and capacitive property of copolymers were much higher after the same polymerization time than that of pure P5MeIn due to the incorporation of EDOT unit into the copolymers. For instance, when the feed ratio was 0.02:0.04 [Fig. 3(d)], the copolymer waves showed greater redox activity compared with pure P5MeIn [Fig. 3(a)]. The values of anodic and cathodic current density were  $7.65$  and  $-7.34 \text{ mA cm}^{-2}$  (Table I), much higher than those of pure P5MeIn ( $0.26$  and  $-0.26 \text{ mA cm}^{-2}$ , respectively). These results indicated that the incorporation of EDOT units had significantly improved the electrochemical activity and capacitive property of pure P5MeIn.

The electrochemical behavior of the copolymer film deposited electrochemically from  $0.02 \text{ mol L}^{-1}$

$5\text{MeIn}$  to  $0.04 \text{ mol L}^{-1} \text{ EDOT}$ , was also studied in monomer free ACN containing  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  (Fig. 4). The steady-state CV represented broad anodic and cathodic peaks. The peak current densities in Figure 4 were proportional to the scan rates (Fig. 4, inset), indicating the reversible redox behavior of copolymer adhered well to the electrode. Furthermore, the anodic and cathodic peak potentials of these films were independent on the scan rates, which suggested that these redox reactions were both reversible and the oxidation reaction was controlled by a charge-transfer step rather than by a diffusion step, even at very high scan rates.<sup>24</sup> In addition, these films can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of materials, indicating high stability of the copolymer. Based on the discussion above, it can be reasonably concluded that the copolymer with better electrochemical behavior was obtained from ACN containing  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ .

### Structural characterizations

P5MeIn film was golden yellow in dedoped state and dark green in doped form. As predicted theoretically,<sup>26</sup> PEDOT film changed its color from transparent pale blue in doped state to opaque red in dedoped form. For the copolymer, its color changed from yellow green in doped state to brown color in dedoped state. The UV-visible spectra of pure P5MeIn, PEDOT and copolymer films deposited at various potentials, were shown in Figure 5. The broadening of the absorbance of the polymer in comparison with the monomers implied the wide molar mass distribution of as-prepared films during the electrosyntheses. The spectra of the P5MeIn films showed a broad absorption from 350 to 450 nm,



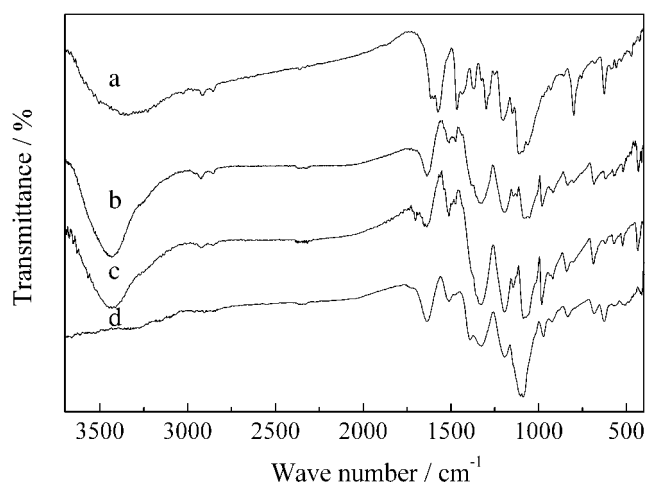
**Figure 5** UV-vis spectra of dedoped (a) P5MeIn, copolymer films prepared at (b)  $1.1 \text{ V}$ , (c)  $1.2 \text{ V}$ , (d)  $1.3 \text{ V}$ , and (e) pure PEDOT respectively.

however there was no obvious absorption of PEDOT in this range [Fig. 5(a)]. On the other hand, the spectra of PEDOT films showed a much broader absorption from 400 to 600 nm [Fig. 5(e)]. Similar to pure P5MeIn and PEDOT, the spectra of copolymer showed characteristic absorptions of both P5MeIn and PEDOT [Fig. 5(b–d)]. According to Figure 5, the obvious absorption of copolymer was located at near 420 nm, being a red shift in contrast to pure PIn due to the introduction of EDOT to copolymer main chain, further certifying the copolymerization phenomenon. The Commission Internationale de l'Eclairage (CIE) 1931 color coordinates of the copolymer were (0.10, 0.54). The CIE coordinates of monochromatic radiation with wavelengths of 470 and 480 nm are (0.124, 0.058) and (0.0913, 0.133), respectively.<sup>27</sup> It is evident that the color-purity enhancement for copolymer resulted from a reduction in the emission with wavelengths,<sup>28</sup> which is in accordance with the UV-visible spectra.

As-formed P5MeIn, PEDOT and copolymers were all insoluble in strong polar solvents such as water and also insoluble in weak polar or nonpolar solvent such as acetone, tetrahydrofuran and acetonitrile, which made it hard to take more complete characterizations.

The composition of the copolymers prepared potentiostatically from ACN + 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> solution containing 0.02 mol L<sup>-1</sup> 5MeIn and 0.04 mol L<sup>-1</sup> EDOT was evaluated by elemental analysis. The found values of elemental analysis result were 59.07% of C, 4.75% of H, 15.07% of S, and 4.15% of N against the calculated values of 60.72, 5.06, 15.42, and 3.37%, respectively. This further confirmed the occurrence of the copolymerization.

Infrared spectra can provide evidence for the characterization the conducting polymer, especially for those insoluble and infusible. P5MeIn, PEDOT, and copolymers prepared potentiostatically at different applied potentials were analyzed by FT-IR spectroscopy, as shown in Figure 6. The bands at 1203, 630 cm<sup>-1</sup> of P5MeIn [Fig. 6(a)] and 1193, 630 cm<sup>-1</sup> of PEDOT [Fig. 6(d)] indicated the presence of perchlorate dopant. According to the spectrum of pure PEDOT [Fig. 6(d)], the bands at 1517, 1480, 1394, and 1330 cm<sup>-1</sup> originated from the stretching modes of C=C and C—C in the thiophene ring.<sup>29</sup> In this region, the absorptions shifted in the spectra of copolymers because of the interaction of benzene ring and thiophene ring during the electrochemical copolymerization. The bands at 1087 cm<sup>-1</sup> [Fig. 6(d)] was assigned to the stretching vibrations of =C—O bond,<sup>30</sup> which can be found in the spectra of the copolymer. This suggested that EDOT units were incorporated into the main chain of the copolymers and higher potentials may favor the incorporation of EDOT units into the copolymer. Furthermore, vibra-

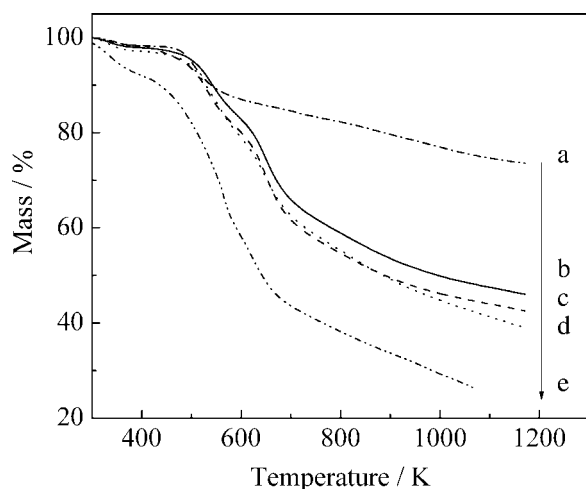


**Figure 6** Infrared spectra of (a) pure P5MeIn, copolymers prepared at (b) 1.1 V, (c) 1.2 V, and (d) pure PEDOT respectively.

tions from the C—S bond in the thiophene ring of PEDOT were shown at 975 and 920 and 836 cm<sup>-1</sup>,<sup>31</sup> which also can be observed in the copolymer. The spectrum of P5MeIn located at 799 and 1059 cm<sup>-1</sup>, evidence for the presence of trisubstituted benzene ring, indicated the occurrence of benzene ring incorporated in the copolymer. The bands located at ~1372 and 1428 cm<sup>-1</sup> [Fig. 6(a)], shifted to 1386 and 1439 cm<sup>-1</sup> in the spectra of copolymer, were assigned to the deformation of the methyl group.<sup>32</sup> In addition, the narrow peak of N—H bond observed in the monomer was broader and shifted to 3400 cm<sup>-1</sup> [Fig. 6(a)], which can also be seen in the spectra of copolymers [Fig. 6(b,c)]. This band, together with the band at 1576 cm<sup>-1</sup>, can be ascribed to the elongation and deformation vibrations of the N—H bond, respectively.<sup>33</sup> This result implied that there was still N—H bond on the dedoped P5MeIn and copolymer backbone. All these features indicated that the copolymerization happened during the potentiostatic electropolymerization of 5MeIn and EDOT, which was consistent with the results of the cyclic voltammetry and the elemental analysis.

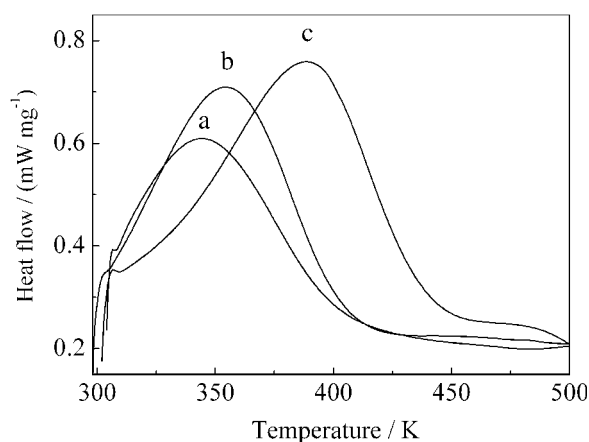
### Thermal analysis

The thermal stability of conducting polymers is very important for their potential applications. TGA is a significant dynamic way of detecting the degradation behaviors. The weight loss of a polymer sample is measured continuously, whereas the temperature is changed at a constant rate. To investigate the thermal stability of copolymers of 5MeIn and EDOT, the thermal properties of P5MeIn, PEDOT, and copolymers obtained at different applied potentials were investigated (Fig. 7). As can be seen from Figure



**Figure 7** TG curves of (a) P5MeIn, copolymer prepared at (b) 1.1 V, (c) 1.2 V, (d) 1.3 V, and (e) PEDOT, respectively.

7(a), before 500 K, a light weight loss of P5MeIn was about 2%, mainly due to the evaporation of water evaporation trapped in the polymer. And only one obvious weight loss of P5MeIn was observed between 510 and 600 K, up to 13% [Fig. 7(a)]. On the contrary, PEDOT began to lose weight at about 350 K [Fig. 7(e)]. When the temperature was up to 1050 K, the residue of P5MeIn and PEDOT were about 75 and 26%, indicating that the thermal stability of P5MeIn was better than PEDOT. The reason for this phenomenon was mainly the incorporation of benzene ring into the polymer backbone. Moreover, it can be seen clearly from Figure 7 that the thermal properties of copolymers prepared at different applied potentials were similar to each other, better than that of pure PEDOT. It can also be seen from this figure that copolymers prepared at 1.1 V



**Figure 8** DSC curves of (a) P5MeIn, (b) copolymer prepared at 1.2 V from ACN + 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> solution containing 0.02 mol L<sup>-1</sup> 5MeIn and 0.04 mol L<sup>-1</sup> EDOT (5MeIn : EDOT = 1 : 2), and (c) PEDOT, respectively. Heating rate: 5 K min<sup>-1</sup>.

showed the slowest degradation rate, indicating that the thermal stability of copolymer prepared at 1.1 V was the best. All these results indicated that the incorporation of 5MeIn units into PEDOT contributed to the improvement of the thermal property of PEDOT.

DSC measurements of the homopolymers/copolymers were performed in the heating range from 300 to 500 K and were conducted at a heating rate of 5 K/min. The obtained results indicate that no first-order phase transition such as melting and crystallization occurs. Figure 8 gave a comparison of DSC curves for P5MeIn [Fig. 8(a)], PEDOT [Fig. 8(c)] and the copolymer [Fig. 8(b)]. The behavior of P5MeIn [Fig. 8(a)], PEDOT [Fig. 8(c)] and the copolymer [Fig. 8(b)] was very different and the corresponding peak temperatures were at 345 K [Fig. 8(a)], 385 K [Fig. 8(c)] and 357 K [Fig. 8(b)], respectively. As the peak temperatures indicate, the DSC scans consist of sharp exothermic peaks indicating that there is a thermal threshold followed by very rapid polymerization.<sup>34</sup> The results correlated well with the reactivity of the corresponding TGA results.

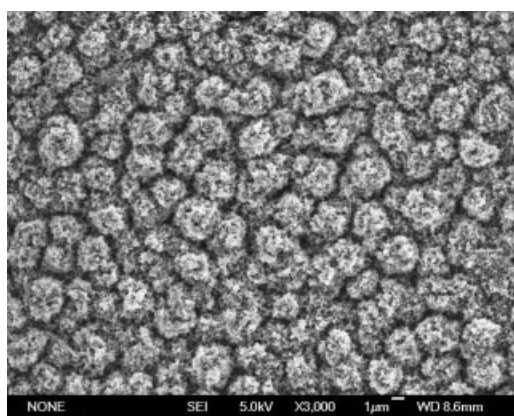
### Conductivity and morphology

The conductivities of P5MeIn, PEDOT, and the copolymers obtained potentiostatically from ACN + 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> solution at different polymerization potentials were shown in Table II. Pure PEDOT exhibited good conductivity, 92.30 S cm<sup>-1</sup>, while the conductivity of P5MeIn was 0.33 S cm<sup>-1</sup>. It can be clearly seen from Table II that the conductivities of the copolymers were between those of pure P5MeIn and PEDOT, indicating that the insert of EDOT units into P5MeIn was helpful to improve the conductivity of P5MeIn, which may be beneficial to extend the applications of P5MeIn. Among the copolymers prepared at different potentials, those electro synthesized at 1.1 V showed the highest conductivity, 8.08 S cm<sup>-1</sup>. This was in accordance with the electrochemical and thermal analysis results. Therefore, 1.1 V was the best potential suitable for the electrocopolymerization of 5MeIn and EDOT.

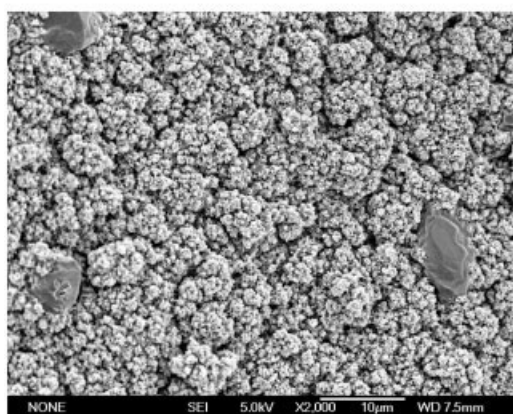
The properties of conducting polymers are strongly dependent on their morphology and struc-

**TABLE II**  
Conductivities of P5MeIn, PEDOT, and Copolymers Obtained at Different Potentials

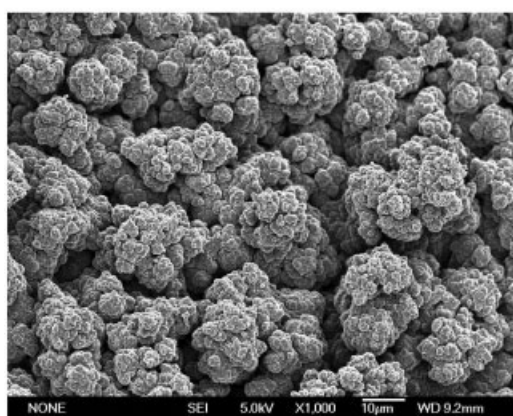
Polymer	Conductivity (S cm <sup>-1</sup> )
P5MeIn	0.33
Copolymer at 1.1V	8.08
Copolymer at 1.2V	5.08
Copolymer at 1.3V	4.79
PEDOT	92.30



(a)



(b)



(c)

**Figure 9** SEM images of (a) pure P5MeIn, (b) copolymers prepared at 1.1 V from the solution ACN + 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> solution containing 0.02 mol L<sup>-1</sup> 5MeIn and 0.04 mol L<sup>-1</sup> EDOT and (c) pure PEDOT.

ture. Therefore, the scanning electron micrographs of P5MeIn, PEDOT, and copolymers obtained at 1.1 V were examined, as illustrated in Figure 8. In this case, pure P5MeIn looked compact with granules arrayed uniformly [Fig. 9(a)]. On the other hand,

the morphology of pure PEDOT was very regular with a growth of aggregates shaped as blossoms [Fig. 9(c)]. Meanwhile, the morphology of the copolymer obtained at 1.1 V showed a grain structure [Fig. 9(b)]. This morphology was between PEDOT and P5MeIn, further confirming the occurrence of copolymerization.

## CONCLUSIONS

A new copolymer obtained from 5MeIn and EDOT was successfully achieved in ACN + 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> solution by the potentiostatic method. The influences of polymerization potential and feed ratio of monomers on the properties of as-formed copolymers were studied in detail and 1.1 V was proved to be the best potential suitable for the electrocopolymerization of 0.02 mol L<sup>-1</sup> 5MeIn and 0.04 mol L<sup>-1</sup> EDOT. Copolymers of 5MeIn and EDOT showed good redox activity and capacitive property. TGA results indicated that the copolymer was better thermally stable than pure PEDOT. It was found that electrical conductivity of copolymer was improved in comparison with that of pure P5MeIn. These properties of copolymer would extend the applications of both P5MeIn and PEDOT.

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