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Electrosynthesis and Characterization of a New Conducting Copolymer from 2'-aminomethyl-3,4-ethylenedioxythiophene and 3,4-ethylenedioxythiophene

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The copolymerization of 2'-aminomethyl-3,4-ethylenedioxythiophene (EDOT-MeNH$_2$) and 3,4-ethylenedioxythiophene (EDOT) was successfully performed electrochemically in acetonitrile (CH_3CN) containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte by direct anodic oxidation of the monomer mixtures. A series of experiments with different monomer feed ratios were carried out to investigate the influence of monomer feed ratio on the electrochemical copolymerization and the overall properties of the copolymer films. As-formed novel copolymers owned both the advantages of poly(2'-aminomethyl-3,4-ethylenedioxythiophene) (PEDOT-MeNH$_2$) and poly(3,4-ethylenedioxythiophene) (PEDOT), *i.e.*, good electrochemical behavior, excellent electrochemical stability, and good thermal stability. Spectroelectrochemistry analysis of copolymer with the feed ratio of 1:1 reflected λ_{max} due to the π–π* transition and polaron band formation was found to be 620 nm and the band gap (E_g) was calculated as 1.67 eV. The structure, thermogravimetry and morphology of the copolymers were investigated by infrared spectroscopy, thermal analysis, and scanning electron microscopy, respectively.

Keywords: conducting polymers; poly(2'-aminomethyl-3,4-ethylenedioxythiophene) (PEDOT-MeNH$_2$); poly(3,4-ethylenedioxythiophene) (PEDOT); electrochemical copolymerization; spectroelectrochemistry

1. INTRODUCTION

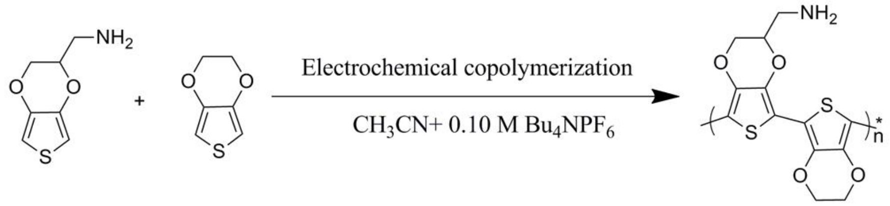
Conjugated polymers (CPs) have attracted considerable attention since they are promising candidates to be amenable for use in a variety of advanced technological applications such as sensors [1-4], light emitting diodes [5,6], photovoltaic cells [7-9], transistors [10], electrochromic devices [11-

13], and optical displays [14] due to their unique attractive properties such as good stability, high conductivity, and low cost. Recently, research on CPs is mainly focused on exploiting novel polymers with outstanding properties as well as further enhancing the performance of available polymers. Generally, the resulting properties of CPs can be controlled via structural modification by introducing some functional groups into the main chain or the pendant chain of the polymer, copolymerizing with some interesting monomer units, or mixing with other materials. As a conventional method, copolymerization is a promising strategy to obtain materials with improved properties or simultaneously possessing the characteristics of both homopolymers. For that matter, many studies and reviews on copolymer preparation, properties, and characterization have been reported [15-20].

Among inherent conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT), an important polythiophene derivative with two electron-donating oxygen atoms on 3,4-positions of thiophene, is a relatively major member in the family of conducting polymers. Recently, PEDOT has become one of the most popular conducting polymers due to its interesting properties, such as moderate band gap, high conductivity, environmental stability upon cycling as well as air, good chemical and electrochemical properties in comparison with other kinds of polythiophene derivatives [21,22]. Its monomer, 3,4-ethylenedioxythiophene (EDOT), has been employed as a building block in the design of copolymers, which incorporate unique properties such as electrochromic behaviour and low band gap. In order to modify the properties of PEDOT, much work have been focused on the electrochemical copolymerization of EDOT with different monomers, such as thiophene [23,24], pyrrole [25,26], indole [27], carbazole [28,29], and pyridine [30].

It is worth noting that, recently, Neal R. Armstrong et al. reported the electrochemical copolymerization and spectroelectrochemical characterization of EDOT with a commonly used EDOT derivative: 2,3-dihydrothieno[3,4-*b*]-1,4-dioxyn-2-yl methanol (EDTM) [31]. 2'-Aminomethyl-3,4-ethylenedioxythiophene (EDOT-MeNH$_2$) is also an important EDOT derivative because the electron-donating -NH$_2$ group has some advantages. First, -NH$_2$ group can increase the band gap of corresponding conducting polymers by the increase of LUMO energy level as an electron-donating group substitution. Furthermore, -NH$_2$ group has an effect on the properties of the corresponding conducting polymers because these polymers can be further modified by functional molecules, which is popular in the electrosynthesis of functional conducting polymers [32-34]. However, to the best of our knowledge, there have been no precedents on electrochemical copolymerization of EDOT-MeNH$_2$ and EDOT so far. By means of electrocopolymerization, it may be beneficial to enhance its conductivity by introduction of EDOT units into EDOT-MeNH$_2$ main chain due to the high conductivity of PEDOT. In the same way, properties of PEDOT may be improved by the incorporation of EDOT-MeNH$_2$ units, such as the solubility, thermal stability and potential further modification of PEDOT.

Herein, EDOT-MeNH$_2$ was copolymerized with EDOT successfully by electrochemical oxidation of the monomer mixtures (Scheme 1). The obtained copolymers were characterized by electrochemistry, spectroelectrochemistry, FT-IR and fluorescence spectra. The thermal stability and morphology of the copolymer were also investigated.



Scheme 1 The electrochemical copolymerization of EDOT-MeNH$_2$ and EDOT in CH$_3$CN + Bu$_4$NPF$_6$ (0.1 M).

2. EXPERIMENTAL SECTION

2.1. Materials

EDOT was purchased from Acros Organics. EDOT-MeNH$_2$ was synthesized as previously described [35]. Dimethyl sulfoxide (DMSO, AR) and acetonitrile (CH$_3$CN, AR) were purchased from Aladdin Chemistry Co. Ltd. Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 99%; Acrocs Organics) was dried under vacuum at 60 °C for 24 h before used.

2.2. Electrochemical synthesis and measurement

The electrochemical experiments were performed in a three electrode system on a model 263A potentiostat/galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. The working and counter electrodes were two platinum wires with diameter of 0.5 mm, respectively, placed 0.5 cm apart. Before each examination, they were carefully polished and cleaned with water and acetone successively. An Ag/AgCl electrode immersed directly in the solution was used as the reference electrode, and it revealed sufficient stability during the experiments. To obtain a sufficient amount of the polymer films for characterization, Indium-tin oxide (ITO) or Pt and stainless-steel sheets with surface areas of 4 and 6 cm^2 each were used as the working and counter electrodes, respectively, and they were carefully polished with abrasive paper (1500 mesh) and then washed with water and acetone successively before each examination. For special analysis, the as-formed polymers were de-doped with hydrazine hydrate for 3 days and then washed repeatedly with water and acetone. At last, they were dried under vacuum at 60 °C for 2 days.

2.3. Characterization

Electrochemical and spectroelectrochemistry were carried out on a model 263A potentiostat/galvanostat (EG&G Princeton Applied Research) and a Cary 50 UV-vis-NIR spectrophotometer under computer control. Spectroelectrochemical measurements were carried out to consider absorption spectra of these polymer films under applied potential. The spectroelectrochemical cell consists of a quartz cell, an Ag/AgCl wire (RE), a Pt wire (CE), and an ITO/glass as transparent working electrode (WE). All measurements were carried out in 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte in CH_3CN. With an F-4500 fluorescence spectrophotometer (Hitachi), fluorescence spectra were determined. Infrared spectra were measured by a Bruker Vertex 70 Fourier-transform infrared (FT-IR) spectrometer with samples in KBr pellets. Scanning electron microscopy (SEM) measurements were taken with a VEGA\\LSU scanning electron microscope (Tescan). Thermogravimetric (TG) analysis was performed with a Pyris Diamond TG/DTA thermal analyzer (PerkinElmer) under nitrogen stream form 290 to 1070 K at a heating rate of 10 K min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Electrochemical copolymerization of EDOT-MeNH$_2$ and EDOT

It is well known that the oxidation potentials of the starting monomers are relatively close with intention to prepare copolymer chain with alternating monomer units [36,37]. In order to investigate the influence of different monomer feed ratios on the electrochemical copolymerization and properties of the copolymer films, and ensure the occurrence of the copolymerization between EDOT-MeNH$_2$ and EDOT, this experiment was carried out in six subordinate groups based on the molar ratio of the monomers. It should be noted here that the background electrolyte is electrochemically inert in the whole potential range.

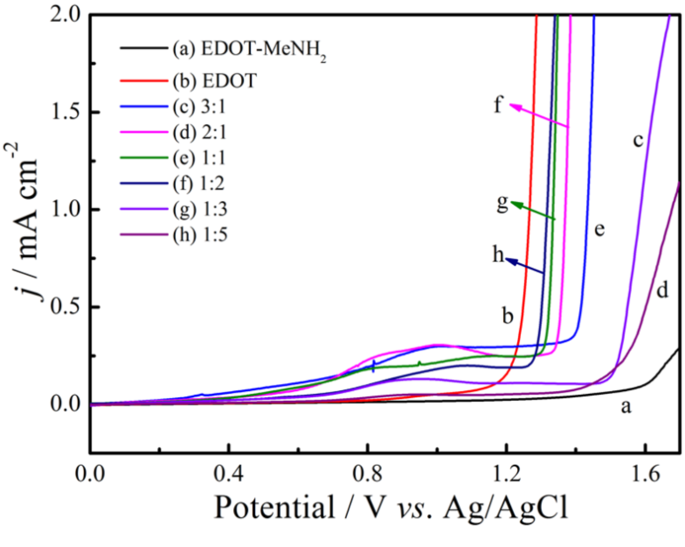


Figure 1. Anodic polarization curves of EDOT-MeNH$_2$ (a), EDOT (b), and monomer mixtures with feed ratios of EDOT-MeNH$_2$/EDOT = 3:1 (c), 2:1 (d), 1:1 (e), 1:2 (f), 1:3 (g) and 1:5 (h) in $CH_3CN + Bu_4NPF_6$ (0.1 M). Potential scan rate 50 mV s^{-1}.

Fig. 1 presented the typical anodic polarization curves of the monomers and monomer mixtures with different feed ratios in the $CH_3CN + Bu_4NPF_6$ (0.1 M). The onset oxidation potentials of EDOT-MeNH$_2$ (a) and EDOT (h) were 1.58 and 1.15 V, respectively. The small difference (0.43 V) between the onset oxidation potentials of EDOT-MeNH$_2$ and EDOT suggested that the copolymerization between the two monomers was possible. A series of experiments with different initial monomer feed ratios were carried out for comparison and to optimize a suitable monomer feed ratio for the copolymerization process. From Fig. 1b-g, the onset oxidation potentials of the monomer mixtures with different feed ratios mainly focused on 1.15-1.58 V between those of EDOT and EDOT-MeNH$_2$. Following decreased concentration of EDOT in the system, the onset oxidation potentials shifted regularly. Therefore, it can be easily deduced that the radical cations of EDOT-MeNH$_2$ and EDOT can form almost simultaneously at the working electrode surface where they can react with each other and form a copolymer [38].

Fig. 2 showed the successive cyclic voltammograms (CVs) of EDOT-MeNH$_2$, EDOT and the monomer mixtured with different feed ratios recorded in the solvent system on platinum electrodes at the potential scan rate of 100 mV s^{-1}. Compared with the monomer of EDOT-MeNH$_2$, as the CV scan continued, conducting polymer films of monomer mixtures with the feed ratios (EDOT-MeNH$_2$/EDOT = 1:1, 1:2, 1:3 and 1:5) were formed on the working electrodes surface. The increase in the redox wave current densities implied that the amount of conducting polymers deposited on the electrode was increasing. Moreover, the obvious potential shift of the wave current density maximum provided information about the increase in the electrical resistance in the polymer film and the overpotential needed to overcome the resistance [39]. While, CVs of the monomer mixtures with the feed ratios of 2:1 and 3:1 showed no apparent redox waves, and after successive potential scans, no polymer film was formed on the electrode at all, indicating that when the concentration of EDOT-MeNH$_2$ was dominated in the monomer mixtures, electropolymerization of the monomers was not successful.

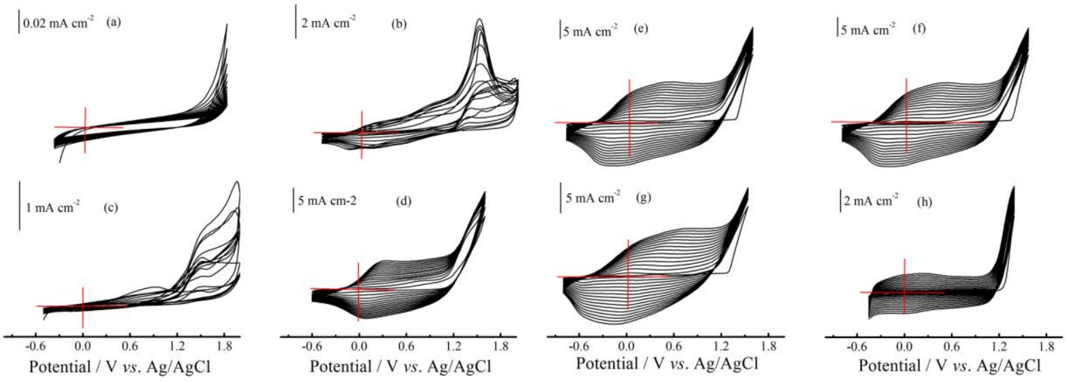


Figure 2. CVs of EDOT-MeNH$_2$ (a), EDOT (h), and monomer mixtures with feed ratios of EDOT-MeNH$_2$/EDOT = 3:1 (b), 2:1 (c), 1:1 (d), 1:2 (e), 1:3 (f), and 1:5 (g) in CH_3CN + Bu_4NPF_6 (0.1 M). Potential scan rate 100 mV s^{-1}.

Fig. 2a exhibited the CVs of EDOT-MeNH$_2$ which was performed between −0.4 and 1.8 V, their redox peaks were not obvious and minute quantity was formed on the electrode. On the contrary, CVs of EDOT recorded in the same medium was quite plump, and EDOT monomer or oligomer could be oxidized and reduced from 0.25 to 0 V, just as illustrated in Fig. 2h. For comparison, CVs of the copolymers deposited in the monomer mixtures with different feed ratios were also illustrated. When the monomer feed ratio of EDOT-$MeNH_2$/EDOT reached 1:1 (Fig. 2d), the mixtures could be oxidized and reduced from 0.4 to 0.12 V. When the concentration of EDOT was dominated in the monomer mixtures, CVs of them were much more similar to those of pure EDOT, indicating that more EDOT units were incorporated into the copolymer film. As the monomer feed ratios (EDOT-$MeNH_2$/EDOT) of the monomer mixtures changed, new redox peaks of the CVs of the copolymer appeared compared with those of EDOT-$MeNH_2$ and EDOT, which indicated that a new copolymer of EDOT-$MeNH_2$/EDOT formed in the system [40] and an appropriate feed ratio of EDOT-$MeNH_2$/EDOT=1:1 was chosen for their copolymerization.

3.2. Optimization of electrical conditions and preparation of the copolymer

To obtain high quality copolymer films, different applied potentials were introduced to ascertain the optimum potentials for copolymerization processes under potentiostatic mode, and the chronoamperometric curves of monomer mixtures were recorded. The chronoamperometric curves of the monomer mixture were shown in Fig. 3. Typically, at applied potentials below the onset oxidation potential, no polymer film was found on the electrode, indicating that polymerization did not occur on the electrode surface due to the low current density. Once the applied potential reached the threshold value, all the electrosynthetic current densities experienced an initial sharp increase followed by a slow decrease. The current density eventually became constant as a result of the uniform deposition of the polymer film on the electrode surface. At relatively high potentials, however, the surfaces of the polymer films became rough, discontinuous, and heterogeneous.

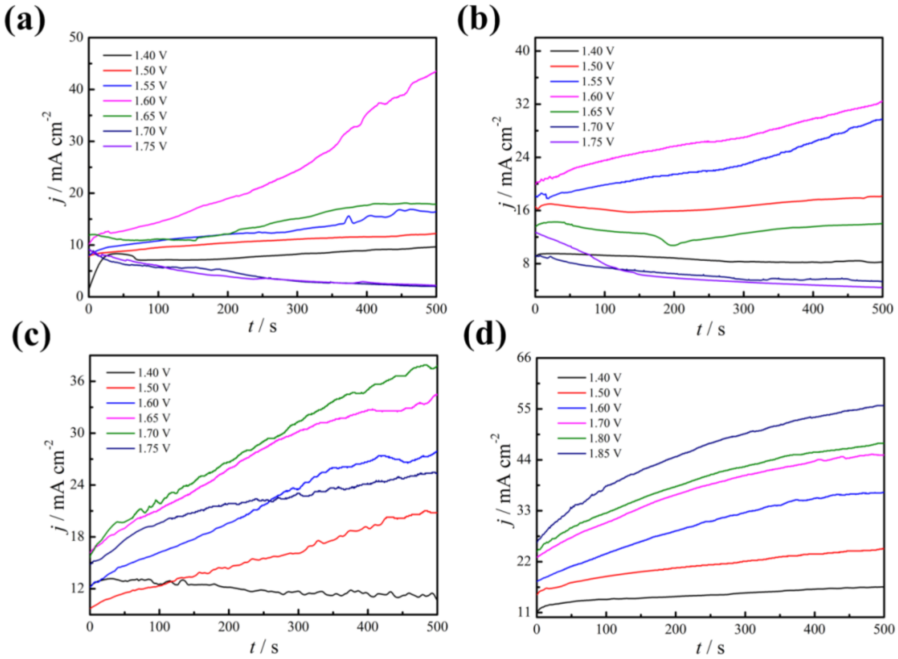


Figure 3. Chronoamperometric curves of the monomer mixtures with feed ratios of EDOT-$MeNH_2$/EDOT = 1:1 (a), 1:2 (b), 1:3 (c), and 1:5 (d) in CH_3CN + Bu_4NPF_6 (0.1 M) on Pt electrodes at different applied potentials for 500 s.

Even worse, some films even fell into the solution from the electrode surface during/after the experiments. This phenomenon was mainly due to significant overoxidation at higher potentials, which led to poor quality films. Considering the overall factors affecting the quality of the as-formed polymer films, such as moderate polymerization rate, negligible overoxidation, regular morphology, and good adherence against the working electrode, the optimized applied potential was 1.6 V *vs*. Ag/AgCl.

3.3. Structural characterization

The formation of copolymer was proved by using FT-IR spectrum. Fig. 4 showed the FT-IR spectra of PEDOT and the copolymer of monomer mixtures with feed ratio of 1:1 in the dedoped state. As the amount of PEDOT-MeNH$_2$ film deposited on the ITO glass was so scarce, the FT-IR spectrum of PEDOT-MeNH$_2$ was not measured. In the spectrum of PEDOT, the bands centered at 2917 cm^{-1} were ascribed to the C-H stretching vibration of methylene; the bands at 1631, 1515 and 1336 cm^{-1} originated from the stretching modes of C=C and C-C in the thiophene rings; and bands at 1197, 1060, 979, and 844 cm^{-1} were attributed to the stretching vibrations of C-O-C and C-S-C, respectively. In the spectrum of the copolymer, the bands at 2969 and 2881 cm^{-1} were associated to the weak characteristic CH$_2$ stretching of the dioxyethlene bridge of the EDOT-MeNH$_2$ molecule, a broad band centered at 3432 cm^{-1} was mainly ascribed to the NH$_2$ asymmetric and symmetric stretching vibration, of which demonstrated the presence of EDOT-MeNH$_2$ units in the copolymer chains. Besides, the bands at 2366 cm^{-1} stemming from the C-H stretching vibration, together with the bands at 1326, 1193, and 979 cm^{-1}, were also observed for EDOT units in the copolymer chains. Therefore, the backbone chains of the prepared copolymer were indeed composed of EDOT and EDOT-MeNH$_2$ units, in accordance with the previously obtained results.

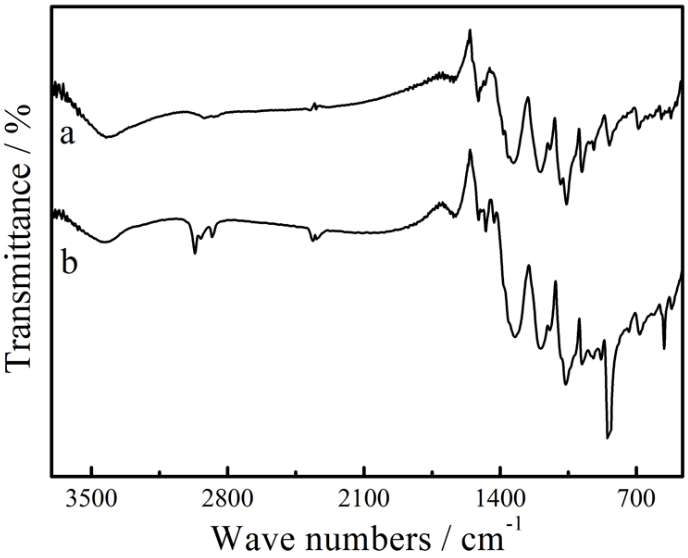


Figure 4. FT-IR spectra of PEDOT (a) and copolymer films deposited with monomer feed ratios of EDOT-MeNH$_2$/EDOT = 1:1 (b) in the dedoped state.

3.4. Electrochemistry of the copolymer film

To obtain a deeper insight into the electrochemical behavior of the as-prepared copolymer, CVs of the PEDOT and copolymer film were measured in the monomer-free solution. Obviously, these polymer films were cycled repeatedly between conducting and insulating states without significant decomposition. Furthermore, exhibited by the insets of Fig. 5, the current densities were proportional to the potential scan rates, indicating a redox couple fixed on the electrode. As can be seen from Fig. 5a, PEDOT synthesized from the system with the concentration of EDOT being 0.01 M was oxidized and reduced from 0.28 to 0.08 V. Fig. 5b-e revealed the CVs of the copolymer films electrodeposited with feed ratios of EDOT-MeNH$_2$/EDOT=1:1, 1:2, 1:3 and 1:5 successively. Specifically, the copolymer film with the feed ratio of EDOT-MeNH$_2$/EDOT=1:1, could be oxidized or reduced from 0.80 to 0.14 V (Fig. 5b).

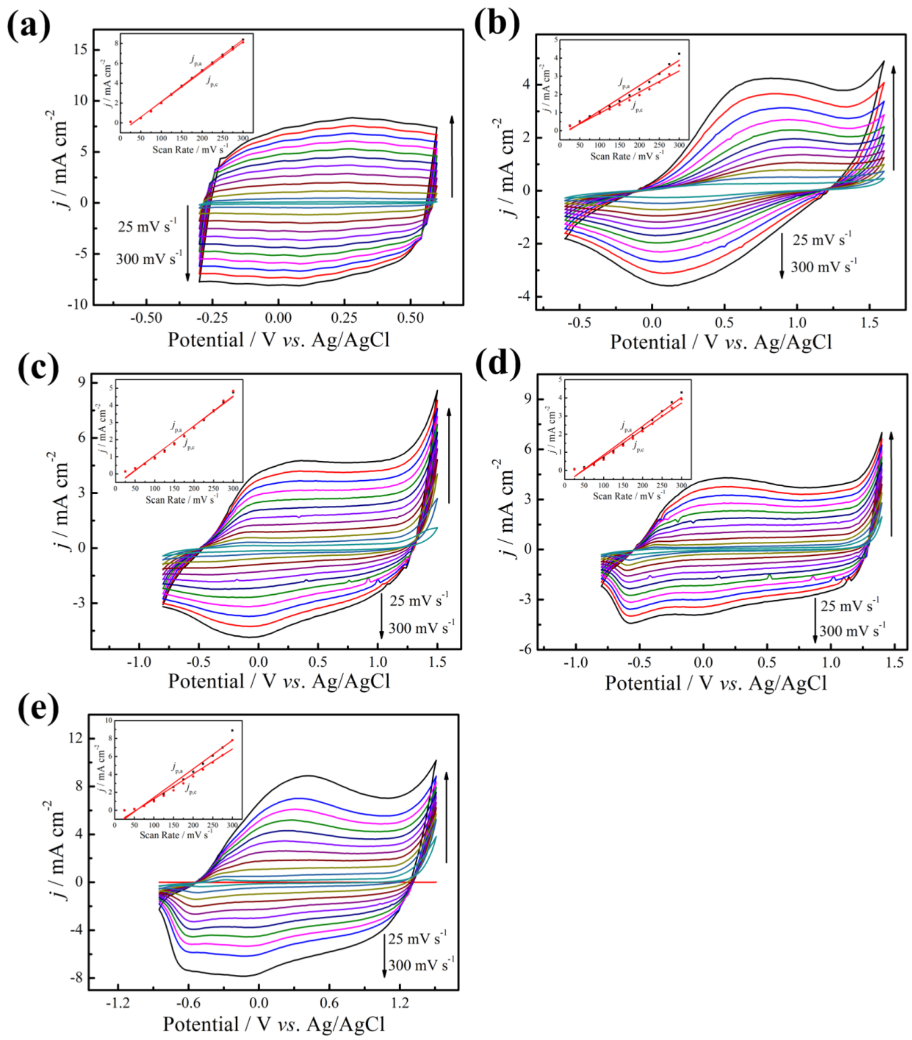


Figure 5. CVs of PEDOT (a) and copolymer films with feed ratios of EDOT-MeNH$_2$/EDOT = 1:1 (b), 1:2 (c), 1:3 (d), and 1:5 (e) recorded in monomer-free CH$_3$CN + Bu$_4$NPF$_6$ (0.1 M) at different potential scan rates. *Insets* plots of redox peak current densities vs potential scan rates. j is peak current density, and $j_{p.a.}$ and $j_{p.c.}$ denote the anodic and cathodic peak current densities, respectively.

With a feed ratio of EDOT-MeNH$_2$/EDOT=1:2, the copolymer exhibited a couple of redox waves at 0.32 and -0.02 V, as shown in Fig. 5c. When the feed ratio changed to 1:5, the redox peaks located at around 0.41 and -0.09 V (Fig. 5e), quite close to the values of PEDOT. The above results demonstrate that the presence of EDOT units indeed plays an important role in improving the electrochemical activity of the prepared copolymer film.

The high stability of one polymer material is essential for its practical application. Therefore, the successive CVs of the copolymer film prepared with different feed ratios of EDOT-MeNH$_2$/EDOT were measured in monomer-free solution at a scan rate of 150 mV s^{-1}. As can be seen in Fig. 6, with the CV scanning continued, the peak current densities slowly diminished and then reached an almost steady state, which might be caused by the partial dissolution of the as-formed oligomer or copolymer into the bulk solution from the electrode surface. The decrease in the peak current density may originate from the initial degradation of the copolymer. After long-term scanning, the CVs still exhibited obvious redox peaks, implying that the prepared copolymer film displayed good redox stability.

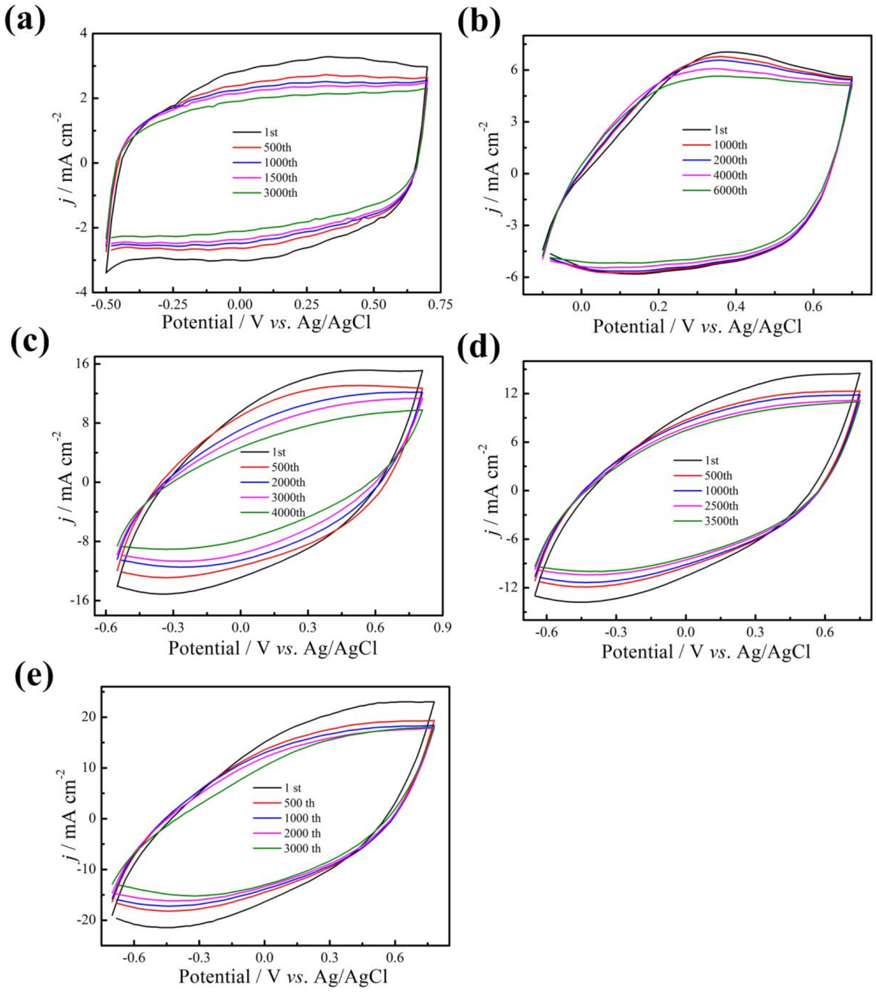


Figure 6. Extended CVs of PEDOT (a) and copolymer films with feed ratios of EDOT-MeNH$_2$/EDOT = 1:1 (b), 1:2 (c), 1:3 (d), and 1:5 (e) in monomer-free CH_3CN + Bu_4NPF_6 (0.1 M) at a potential scan rate of 150 mV s^{-1}.

3.5. Spectroelectrochemistry

The best way of examining the changes in optical properties of conducting polymers upon applied voltages is via spectroelectrochemistry. It also gives information on the electronic structure of the polymer such as band gap (E_g) and the intergap states that appear upon doping. PEDOT and copolymer films were potentiostatically synthesized at 1.3 V and 1.6 V respectively on ITO electrodes. Electrolyte solutions were composed of CH_3CN + Bu_4NPF_6 (0.1 M) and 0.01 M EDOT for the synthesis of PEDOT, and copolymers containing different proportions of EDOT were obtained using different monomer feed ratios. The spectroelectrochemical properties of the resultant polymers (after being rinsed with acetonitrile) were studied by applying potentials for PEDOT and copolymer in a monomer-free CH_3CN + Bu_4NPF_6 (0.1 M) medium.

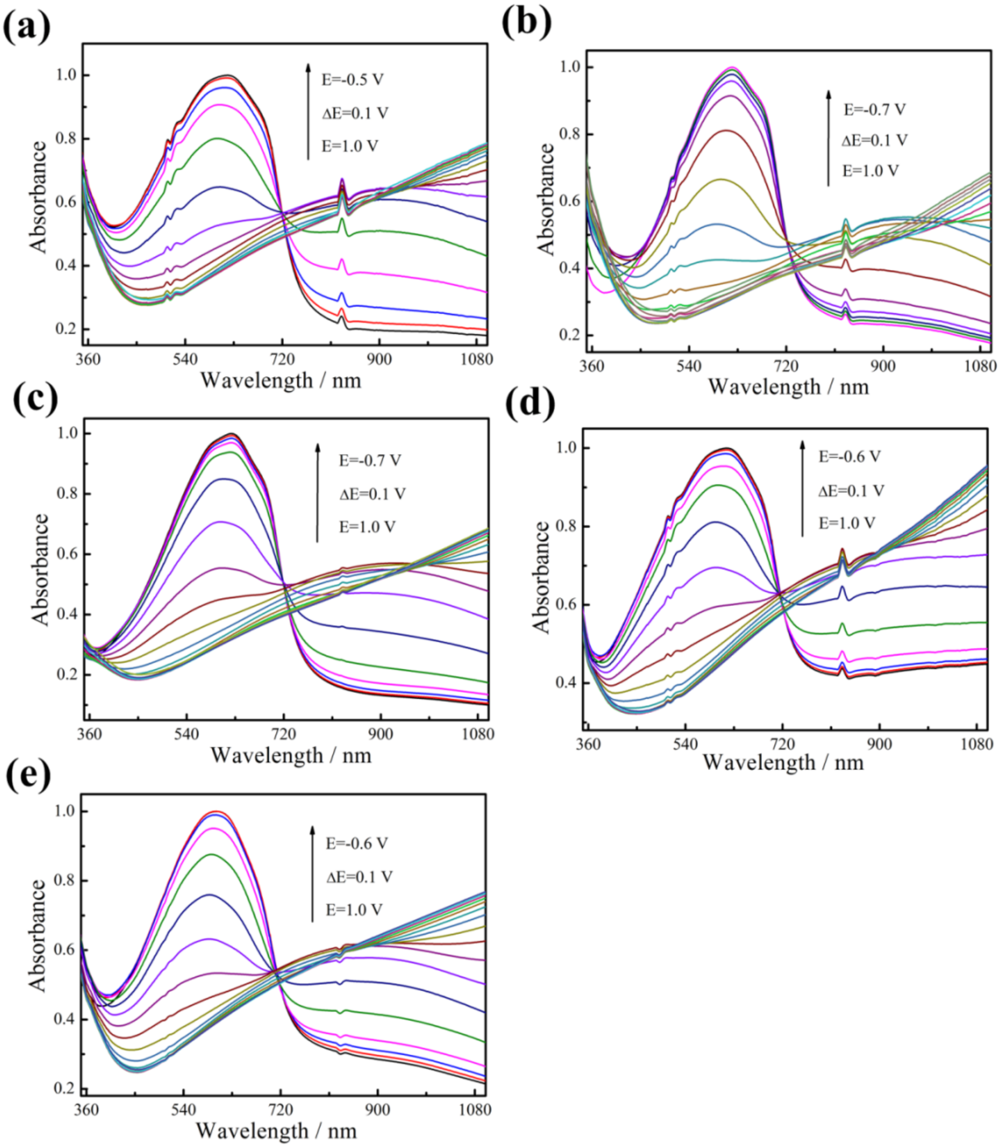


Figure 7. Spectroelectrochemistry of PEDOT (a) and copolymer films with feed ratios of EDOT-$MeNH_2$/EDOT = 1:1 (b), 1:2 (c), 1:3 (d), and 1:5 (e) on ITO-coated glasses in monomer-free CH_3CN + Bu_4NPF_6 (0.1 M) at applied potentials.

Spectroelectrochemical spectra of PEDOT and copolymers were illustrated in Fig. 7. The onset energy for the π-π* transition (E_g) was 1.65 eV, and λ_{max} was found to be 615 nm for the PEDOT. Optoelectrochemical spectra of copolymer film at applied potentials were shown in Fig. 7b-e. The λ_{max} value for the π-π* transition in the neutral state of these copolymers were found to be about 620 nm and E_g were 1.67 eV, which were similar to that of PEDOT. Therefore, with the amount of EDOT increases in the copolymer, the maximum wavelength of the π-π* transition changed a little and the E_g for these copolymers (measured as the onset of the π-π* transition) decreased indistinctly.

3.6. Fluorescence property

The fluorescence emission spectra of PEDOT and the copolymers in the dedoped state with monomer feed ratios of EDOT-MeNH$_2$/EDOT=1:1, 1:2, 1:3, and 1:5, dissolved in DMSO were illustrated in Fig. 8. PEDOT exhibited a strong emission peak at about 602 nm (Fig. 8a). For the copolymers, the corresponding fluorescence spectra were a little red shift compared with that of PEDOT, indicating that there were EDOT-MeNH$_2$ units inserting into the copolymer or oligomer chains. The intrachain energy transfer in the copolymer or the intrachain interaction between the polymer chains dissolved in DMSO were less efficient [41].

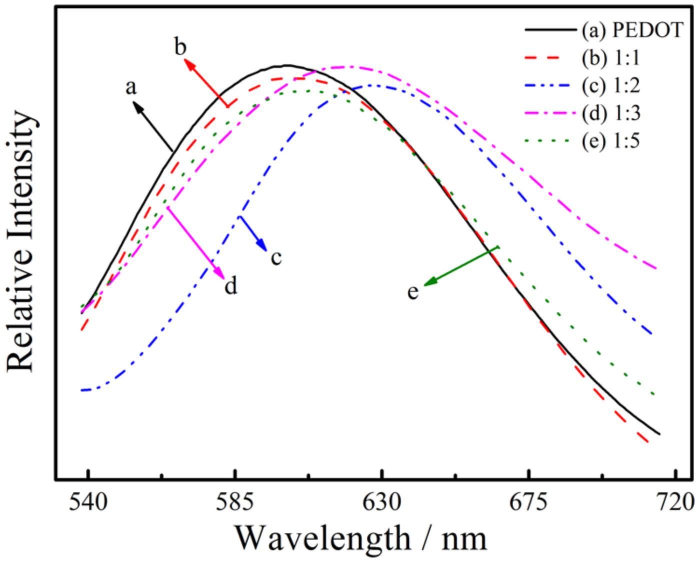


Figure 8. Fluorescence emission spectra of dedoped PEDOT (a) and copolymer films deposited with feed ratios of EDOT-MeNH$_2$/EDOT = 1:1 (b), 1:2 (c), 1:3 (d), and 1:5 (e) in DMSO.

3.7. Morphology

The properties of conducting polymers are strongly dependent on their morphology and structure. Therefore, the surface morphologies of the as-prepared PEDOT, PEDOT-MeNH$_2$, and the copolymer films with the feed ratio of 1:1 deposited on ITO glass surface were examined by scanning electron microscopy (SEM), as illustrated in Fig. 9. The morphology of pure PEDOT was very regular with a growth of aggregates shaped as blossoms (Fig. 9a). Fig. 9b revealed the morphology of PEDOT-MeNH$_2$ film and it emerged rough morphology. The SEM image of the copolymer film with the feed ratios of 1:1 was exhibited in Fig. 9c, and a number of clusters could be observed in the surface of the copolymer film, different from those of PEDOT (Fig. 9a) and PEDOT-MeNH$_2$ (Fig. 9b) films. Therefore, the morphological difference between PEDOT and copolymer was another evidence for the copolymer formation.

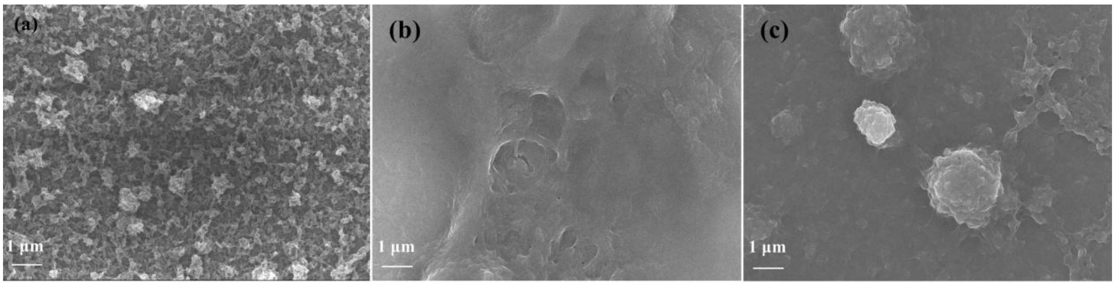


Figure 9. SEM images of PEDOT (a), PEDOT-MeNH$_2$ (b), and copolymer film with feed ratio of 1:1 (c) electrochemically synthesized in $CH_3CN + Bu_4NPF_6$ (0.1 M) on ITO glasses in the doped state.

3.8. Thermal analysis

It is well known that the thermal property of conducting or semiconducting polymers is quite important for their potential applications.

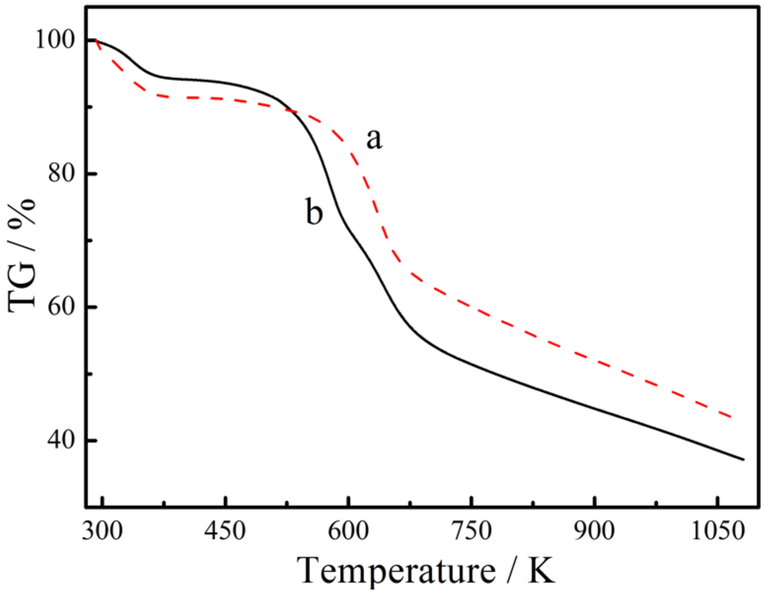


Figure 10. Thermogravimetric (TG) curves of PEDOT (a) and copolymer films deposited with monomer feed ratios of EDOT-MeNH$_2$/EDOT = 1:1 (b) in $CH_3CN + Bu_4NPF_6$ (0.1 M).

To investigate the thermal property of these polymers and copolymers, thermogravimetric analytical (TG) experiments were performed under a nitrogen stream at a heating rate of 10 K min^{-1}, as shown in Fig. 10. For PEDOT (Fig. 10a), there was a prominent decomposition at 641 K, which might be attributed to the degradation of some oligomers and the decomposition of the skeletal PEDOT back bone structure. For the copolymer, with the feed ratios of 1:1 (Fig. 10b), there were two prominent decompositions at 578 and 643 K. The former might be attributed to the degradation of some oligomers and the latter one was caused by the decomposition of the polymer back bone structure [42]. The above mentioned implied that the incorporation of EDOT and EDOT-$MeNH_2$ units into the copolymer chains had influence on the thermal property of the copolymer. All these results demonstrated that the copolymers had good and favorable thermal stability for their potential applications.

4. CONCLUSIONS

A novel high-quality conducting copolymer (P(EDOT-$MeNH_2$-EDOT)) was prepared by electrochemical polymerization of EDOT-$MeNH_2$ and EDOT in CH_3CN + Bu_4NPF_6 (0.1 M) solution by direct anodic oxidation of the monomer mixtures. The influences of polymerization potential and feed ratio of monomers on the properties of as-formed copolymers were studied in detail. The chemical structure was analyzed with the help of FT-IR. The thermal analysis result indicated the high thermal stability of the copolymer. Spectroelectrochemistry indicated that the copolymer has good electrochromic properties. These properties of copolymers may extend the applications of both PEDOT-$MeNH_2$ and PEDOT.

ACKNOWLEDGEMENTS

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