

ELECTROSYNTHESES OF FREE-STANDING POLY(THIOPHENE-3-ACETIC ACID) FILM IN MIXED ELECTROLYTES OF BORON TRIFLUORIDE DIETHYL ETHERATE AND TRIFLUOROACETIC ACID*

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Abstract High quality free-standing poly(thiophene-3-acetic acid) (PTAA), a water-soluble polythiophene derivative, was successfully electrosynthesized in boron trifluoride diethyl etherate (BFEE) + 25% (by volume) trifluoroacetic acid (TFA) at lower potential (0.38 V versus Pt). The carboxyl group makes PTAA highly soluble in water, facilitating its potential application as a blue-light-emitting material. PTAA films with conductivity of 7 S cm^{-1} obtained from this medium showed better redox activity and thermal stability. The structure and morphology of the polymer were studied by UV-Vis, FT-IR, $^1\text{H-NMR}$ spectra and scanning electron microscopy, respectively.

Keywords: Electropolymerization; Conducting polymer; Poly(thiophene-3-acetic acid); Free standing film.

INTRODUCTION

Polythiophene and its derivatives have attracted considerable attention over the past 20 years, mainly because of their remarkable solid-state properties, including their stability in the atmosphere, high conductivity and ease in forming free-standing and high strength film^[1–3]. Generally, stiff conjugated polymers with increasing conjugation efficiencies are intractable and insoluble. Therefore, water-soluble semiconducting polymers have attracted much attention^[4]. The water-soluble polymers can be synthesized by the incorporation of polar functional groups, such as carboxyl groups, anionic sulfonates and quaternary ammonium salts, onto the polymer backbone. Most importantly, functional semiconducting polymers can provide binding sites for covalent immobilization of enzymes^[5, 6]. Poly(3-thiophene acetic acid) (PTAA) is one of the most promising conducting polymers because it can be used in several fields from optical sensors^[7, 8] to chemically modified electrodes^[9–11]. Therefore, PTAA has received a significant share of attention in the past several years.

To the best of our knowledge, PTAA was widely synthesized through chemical oxidation^[12, 13] except few work concerning direct electrochemical oxidation^[14] of thiophene-3-acetic acid (TAA). Compared with chemical oxidation, PTAA film obtained by electrochemical oxidation of TAA has its special advantages. PTAA can be deposited on the electrode surface in one step without further purification. The size and thickness of the film can be controlled easily by the current and deposit time. Up to now, the electrodeposition of PTAA film was mainly performed in the neutral solvents, such as CHCl_3 and acetonitrile, using ClO_4^- or BF_4^- as the supporting

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electrolyte^[14, 15]. However, the oxidation of TAA requires very high potential in neutral solvents, and the polymer has not been characterized in detail. It is well-known that high oxidation potential generally makes the electropolymerization of aromatic monomers quite difficult and also leads to some side reactions. Furthermore, the conducting polymer film produced on the electrode is easily overoxidized during further electropolymerization. The monomer in an exact solvent can be electropolymerized at a lower potential, which is benefit for the quality of the produced polymer film. Boron trifluoride diethyl etherate (BFEE) is known to be electrochemically stable over a wide potential range and is always chosen as the solvent for electropolymerization. The ionic conductivity of freshly distilled BFEE can be as high as about $400 \mu\text{S cm}^{-1}$. The BFEE system has been proved to be a good medium not only in electrosynthesis of high quality conducting polymers but also in the study of conduction mechanisms^[16]. Recently, investigations on the electrochemical polymerization of fused ring compound in BFEE, such as 2,2'-dinaphthyl ether^[17], 1-nitropyrene^[18], (S)-(-)-1,1'-bi-2-naphthol dimethyl ether^[19], 1,1'-binaphthyl^[20], 9,9-difluorofluorene^[21], *etc.* also proved the property improvement of corresponding conducting polymers. The interaction among the middle strong Lewis acid, BFEE and the aromatic monomers can lower their oxidation potentials. The catalytic effect of BFEE facilitates the formation of high quality free-standing polymer films. It also should be noted here that the addition of trifluoroacetic acid (TFA) into BFEE can further decrease the oxidation potentials of the monomers and improve the properties of corresponding polymers^[22–32]. The addition of TFA into BFEE can increase the conductivity of the electrolyte significantly. As far as we know, the mixed electrolyte containing BFEE and TFA had never been used for electrochemical polymerization of TAA.

On the basis of the considerations described above, the mixed electrolytes of BFEE and TFA were chosen for the electrochemical polymerization of TAA. The high-quality and water soluble PTAA film has been electropolymerized successfully in the mixed electrolytes of BFEE and TFA. The electrochemistry, optical property and structural characterization of PTAA are presented in detail.

EXPERIMENTAL

Materials

BFEE (47%–47.7%) purchased from Sinopharm Chemical Reagent Co., Ltd. was distilled and stored at -20°C before use. Tetrabutylammonium tetrafluoroborate (TBATFB, J&K chemical. Ltd, 95%) was dried in vacuum at 60°C for 24 h before use. Thiophene-3-acetic acid (TAA, J&K Scientific Ltd., 98%) was used as received. TFA was obtained from Sinopharm Chemical Reagent Co. Ltd. Commercial HPLC grade acetonitrile (ACN, made by Tianjin Guangcheng Chemical Reagent Co. Ltd) was used directly without further purification.

Electrosyntheses of PTAA Films

Electrochemical synthesis and measurements were performed in a three-electrode cell using Zennium electrochemical workstation (ZAHNER, Germany). All electrodes used in the cyclic voltammetry experiments were platinum wires ($\phi 0.5 \times 20 \text{ mm}$). To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 cm^2 each were employed as the working and counter electrodes, respectively. Electrodes were polished carefully with abrasive paper (2000 mesh) and cleaned by water and acetone before each examination. A typical electrolyte solution was BFEE + 25% TFA (by volume) containing 0.1 mol L^{-1} TAA. The electrochemical dedoping of PTAA films was performed at a constant potential of 0 V in a monomer free BFEE solvent until the current density was close to zero. All potentials were referred to a platinum electrode (Pt).

Characterizations

The conductivity of as-formed PTAA films was measured by the conventional four-probe technique. UV-Vis spectra were measured using a PERSEE TU-1901 spectrophotometer. Infrared spectra (FT-IR) were measured using a PE 1600 spectrometer with KBr pellets. The fluorescence spectra were determined with an Edinburgh Instruments Ltd-FLS920 fluorescence spectrophotometer. The ^1H -NMR spectra were recorded with a Bruker AV 400 NMR spectrometer and D_2O was used as the solvent. Gel permeation chromatography (GPC)

measurements of the soluble polymers were performed in H₂O with a Waters Breeze GPC system. Mass spectrometry was carried out on a Bruker amaZon X mass spectrometer. The thermogravimetric analysis was performed with a thermal analyzer of PE Diamond TG/DTA. Scanning electron microscopy (SEM) was performed using a QUANTA FEG 250 instrument.

RESULTS AND DISCUSSION

Electrochemical Polymerization of TAA

Figure 1 shows the anodic polarization curves of TAA in different electrolytes. The oxidation onset of TAA is initiated at 0.47 V versus Pt in pure BFEE. The addition of 25% TFA into BFEE decreases the onset of oxidation of TAA greatly to about 0.37 V versus Pt. These values are much lower than that of TAA in ACN containing 0.1 mol L⁻¹ TBATFB (1.26 V versus Pt), as shown in Fig. 1. It is seen obviously that the oxidation potential of TAA in BFEE+ 25% TFA is the lowest. The addition of TFA into BFEE may lead to the formation of π -complexes between the monomer and the strong acid, which reduces the resonance of the aromatic ring and synchronously enhances the stability of the radical cations^[33]. The lower the oxidation potential is, the fewer defects the polymer film has. Therefore, BFEE containing 25% TFA (by volume) is more appropriate for the electrochemical polymerization of TAA.

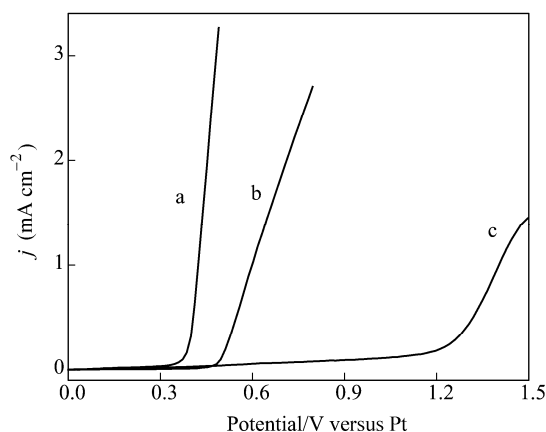


Fig. 1 Anodic polarization curves of 0.1 mol L⁻¹ TAA in BFEE + 25% TFA (by volume) (a), in pure BFEE (b) and in ACN + 0.1 mol L⁻¹ TBATFB (c) Scanning rates: 25 mV s⁻¹

The successive cyclic voltammograms (CVs) of 0.1 mol L⁻¹ TAA in different electrolytes are illustrated in Fig. 2. As can be seen from this figure, the CVs of TAA in BFEE shows characteristic features as other conducting polymers, such as polythiophene and polypyrrole, during potentiodynamic syntheses. The increase in the redox wave currents implies that the amount of polymer on the electrode is increasing. When the introduction of TFA is 25% (Fig. 2a), the peak current is larger than that in pure BFEE (Fig. 2b). The introduction of TFA into BFEE makes the polymerization rate increase gradually mainly due to the decrease of the oxidation potential of the monomer. The broad redox waves of as-formed PTAA film in BFEE + 25% TFA may be ascribable to the wide distribution of the polymer chain length^[34]. The shift of the peak potential provides information about the increase of the electrical resistance in the polymer film. Therefore, the over-potential is needed to overcome the resistance. As the CVs scan continues, the color of the solution close to the working electrode changes slightly from colorless to dark, indicating that part of the monomer is oxidized into oligomers which are dissolved or dispersed in the solvent. Simultaneously, a dark polymer film is also formed on the working electrode surface. All these phenomena indicate that a good PTAA film has been formed on the working electrode in BFEE+ 25% TFA electrolytes.

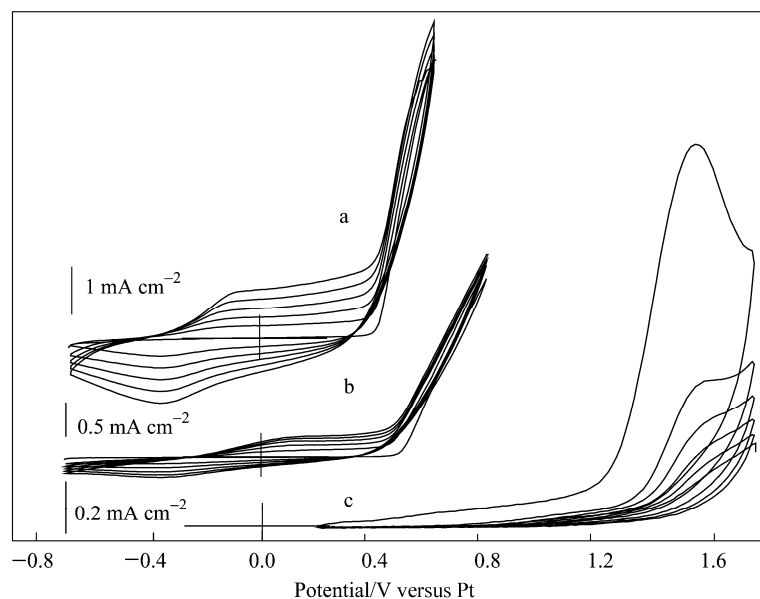


Fig. 2 Cyclic voltammograms of 0.1 mol L⁻¹ TAA in BFEE + 25% TFA (by volume) (a), in pure BFEE (b) and in ACN + 0.1 mol L⁻¹ TBATFB (c) Scanning rates: 25 mV s⁻¹

In contrast, the CVs of TAA in ACN + 0.1 mol L⁻¹ TBATFB are recorded as shown in Fig. 2(c). The anodic peak currents decrease quickly with increasing CVs scan numbers. There are not apparent redox waves and no polymer is formed on the electrode. It is hard for TAA to be polymerized on the electrode in ACN/TBATFB system by the potentiodynamic method. Therefore, the following work was concentrated on the electrosynthesis and characterizations of PTAA film prepared in BFEE + 25% TFA.

Electrochemical Activity of PTAA Film

To get insight into the electrochemical behavior of PTAA films, the electrochemical properties of the PTAA film deposited electrochemically from BFEE+ 25% TFA solution were studied in monomer-free BFEE+ 25% TFA (Fig. 3). As shown in Fig. 3, the modified electrode represents the steady-state and broad redox peaks (both anodic and cathodic) in the monomer-free electrolytes, which can be due to the fact of slow diffusion of the counterions inside the film, changes of the film capacitance and the presence of a wide distribution of the polymer chain length resulting from coupling defects distributed statistically. The peak current densities is proportional to the potential scanning rates (inset of Fig. 3), indicating that the redox process is non-diffusional and the electroactive polymer is well adhered to the working electrode surface. Furthermore, the modified electrode could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials, indicating high stability of the polymer. The polymer film could be oxidized and reduced from 0.42 V (anodic peak potential, E_a) to 0.03 V versus Pt (cathodic peak potential, E_c) in monomer-free electrolyte. All of these results indicate that the as-formed PTAA film shows good redox activity^[35, 36].

The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of PTAA were determined from the onset of reduction and oxidation potentials, $E_{\text{onset}}^{\text{re}}$ and $E_{\text{onset}}^{\text{ox}}$, respectively, by assuming the energy level of ferrocene/ferrocenium (Fc) to be -4.8 eV below vacuum. The empirical equations are as follows^[37, 38]:

$$E_{\text{LUMO}} = -e(E_{\text{onset}}^{\text{re}} + 4.8) \text{ V} \quad (1)$$

$$E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{ox}} + 4.8) \text{ V} \quad (2)$$

$$E_g^{\text{ec}} = E_{\text{LUMO}} - E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{re}} - E_{\text{onset}}^{\text{ox}}) \text{ V} \quad (3)$$

As shown in Fig. 4, $E_{\text{onset}}^{\text{re}}$ and $E_{\text{onset}}^{\text{ox}}$ of PTAA in ACN containing 0.1 mol L⁻¹ TBATFB are observed at -1.63 V and +0.19 V versus Pt, respectively. Therefore, the electrochemical band gap (E_g^{ec}) can be estimated to be 1.82 eV.

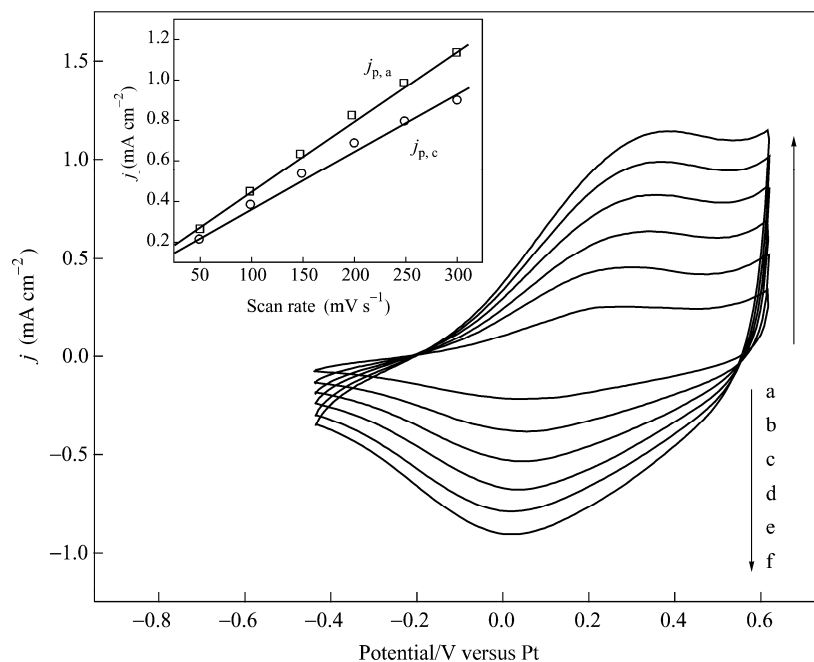


Fig. 3 Cyclic voltammograms of PTAA film in BFEE + 25% TFA (by volume) at potential scan rates of 50 mV s⁻¹ (a), 100 mV s⁻¹ (b), 150 mV s⁻¹ (c), 200 mV s⁻¹ (d), 250 mV s⁻¹ (e) and 300 mV s⁻¹ (f). The PTAA film was synthesized electrochemically in BFEE + 25% TFA (by volume) at a constant applied potential of 1.20 V; $j_{p,a}$, $j_{p,c}$ are defined as the anodic peak current densities, and the cathodic peak current densities, respectively.

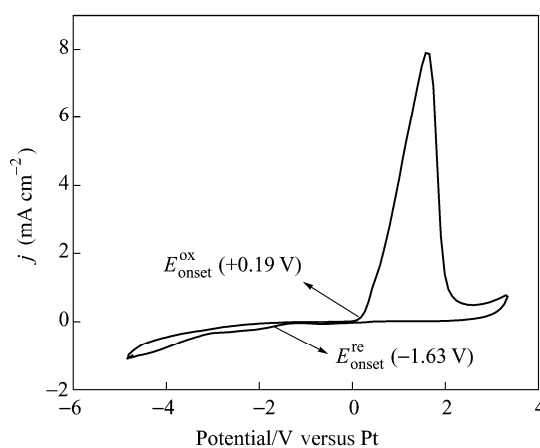


Fig. 4 Cyclic voltammograms of PTAA film in ACN + 0.1 mol L⁻¹ TBATFB at a potential scan rate of 50 mV/s. The PTAA film was synthesized electrochemically in BFEE + 25% TFA (by volume) at a constant applied potential of 1.20 V.

Structure Characterization

The TAA and dedoped PTAA film are both soluble in H₂O. The UV-Vis spectra of TAA and dedoped PTAA in H₂O are shown in Fig. 5. In Fig. 5(a), the spectrum of monomer shows λ_{max} absorption at 237 nm. While in Fig. 5(b), the spectrum of the dedoped PTAA film shows λ_{max} absorption at 440 nm. The red shift of peak of PTAA compared with that of the monomer reflects the higher conjugation length of the backbone. Results indicate polymer with a higher molecular mass has been formed successfully with broad molar mass distribution^[39]. On the other hand, the band gap of PTAA calculated from the onset of the optical absorption spectra (about 660 nm) was roughly 1.88 eV ($E_{\text{g}}^{\text{opt}} = 1241/\lambda_{\text{onset}}$)^[28]. This value was in accordance with E_{g}^{ec} (1.82 eV) determined from the electrochemical method. The band gap of PTAA obtained here was lower than that of PTAA prepared in tetrabutylammonium perchlorate (2.4 eV)^[14]. Therefore, PTAA films with more region regularity were formed in BFEE rather than in tetrabutylammonium perchlorate.

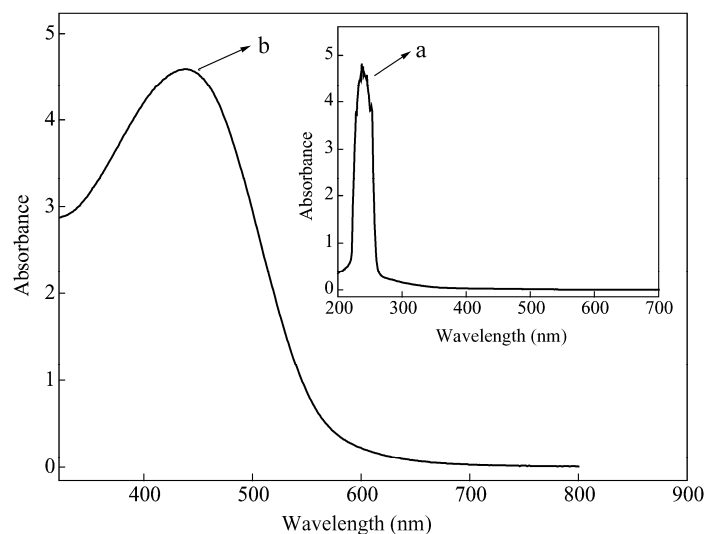


Fig. 5 UV-Vis spectra of TAA (a) and dedoped PTAA (b) prepared potentiostatically at 1.2 V versus Pt from BFEE+25% TFA
Solvent: H₂O

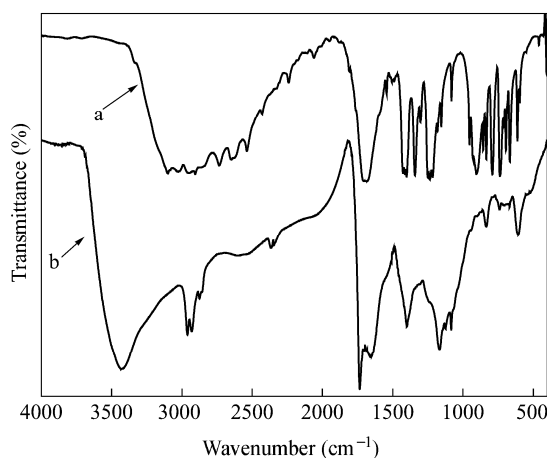


Fig. 6 FT-IR spectra of TAA (a) and dedoped PTAA film (b)

Vibrational spectra can provide further structural information. The transmission infrared spectra of the monomer and doped PTAA film are shown in Fig. 6. According to the spectrum of the monomer, the band at

2951 cm^{-1} is ascribed to the aliphatic C—H stretching vibration. The band at 1418 cm^{-1} is the skeleton vibration of thiophene ring. The intense band at 1702 cm^{-1} is the characteristic absorption of carboxylic group, which is broader and shifts to 1731 cm^{-1} in the spectrum of the dedoped PTAA film. Results imply that there are still —COOH groups on the dedoped PTAA backbone. The absorption of the aromatic C—C emerges at 1656 cm^{-1} . Absorption vibration band at 832 cm^{-1} is assigned to C β —H out-of-plane deformation mode. The C α —H out-of-plane deformation vibration is at 780 cm^{-1} . After polymerization, the C α —H out-of-plane deformation vibration at 780 cm^{-1} disappears. Results imply that the polymerization mainly occurs at C(2) and C(5) positions (in the inset of Fig. 7).

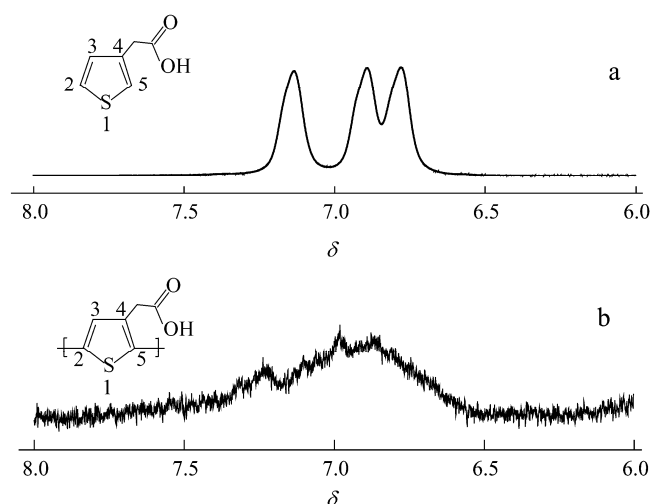


Fig. 7 ^1H -NMR of TAA (a) and dedoped PTAA film (b) prepared from BFEE+25% TFA
Solvent: D_2O

To further investigate the polymer structure and the polymerization mechanism of TAA, the ^1H -NMR spectra of TAA (Fig. 7a) and dedoped PTAA obtained from BFEE+25% TFA (Fig. 7b) were recorded in D_2O . The proton lines of the polymer are much broader than those of the monomer due to the wide molar mass distribution or the complex structure of the polymer. In Fig. 7(a), three peaks at $\delta = 7.13$, 6.89, and 6.78 are assigned to the protons at the C(2), C(3), and C(5) positions (in the inset of Fig. 7), respectively^[40, 41]. In the same region, there is only one broad peak at $\delta = 6.98$ for the polymer, corresponding to the C—H bond at the C(3) position. The chemical shift of the C(3)—H moving to lower field also confirms the formation of a conjugated delocalizing structure. These results indicate that the polymerization positions are C(2) and C(5) (α — α coupling), in good agreement with the FT-IR results. Meanwhile, the chemical shifts of the protons moving to lower fields also confirmed the formation of a conjugated delocalizing structure.

The fluorescence emission spectra of the monomer and the dedoped polymer are determined in H_2O , as shown in Fig. 8. According to Fig. 8, the obvious emission peak of TAA can be found at 309 nm, while the obvious emission peak of PTAA can be found at 581 nm. Large red shifts between the monomer and the polymer can be clearly seen from the figure, which is mainly attributable to the elongation of the polymer's delocalized π -electron chain sequence. The wide peak distribution can be ascribed to the wide molar mass distribution of PTAA, in accordance with UV-Vis spectra and ^1H -NMR results. These results indicate that the water-soluble PTAA film has electrosynthesized successfully from BFEE+TFA and it is a good blue light emitter.

During the potentiostatic process, the color of electrolyte containing TAA darkened with the progress of polymerization reaction, which indicated that soluble TAA oligomers formed during anodic oxidation. With the polymerizing propagation, part soluble oligomers deposited on the working electrode with the elongation of the

main chain. However, there were still part oligomers diffusing from the electrode into the bulk solution. As a result, the color of the bulk solution became darkened. In order to investigate the reproducibility of synthesized PTAA, the molecular weights of PTAA sample obtained under the same conditions were determined by gel permeation chromatography (GPC). GPC measurements in H_2O , using polyethyleneglycol as a standard, indicate a weight-average molecular weight (M_w) of approximately 2600 with a polydispersity of 1.59. The composition of soluble PTAA film in H_2O was characterized by mass spectrometry, as shown in Fig. 9. As can be seen, the mass spectra revealed that the soluble polymer from BFEE + 25% TFA was mainly constituted of tetramers (m/z 560.7), hexamers (m/z 840.7) and undecamers (m/z 1541.2). These results indicated that the soluble polymer was composed of relatively long-chain oligomers (4–11 repetitive units), well in accordance with cyclic voltammograms.

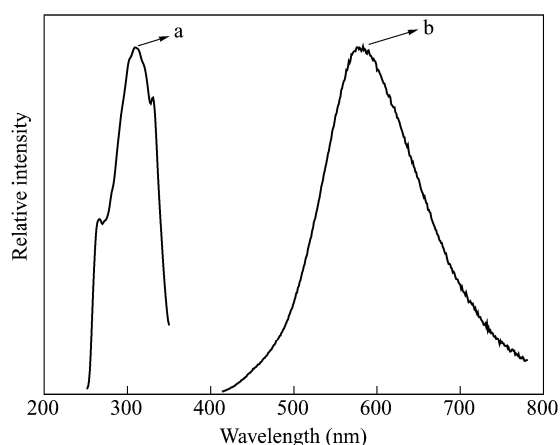


Fig. 8 Emission spectra of TAA (a) and dedoped PTAA film (b) prepared from BFEE + 25% TFA
Solvent: H_2O

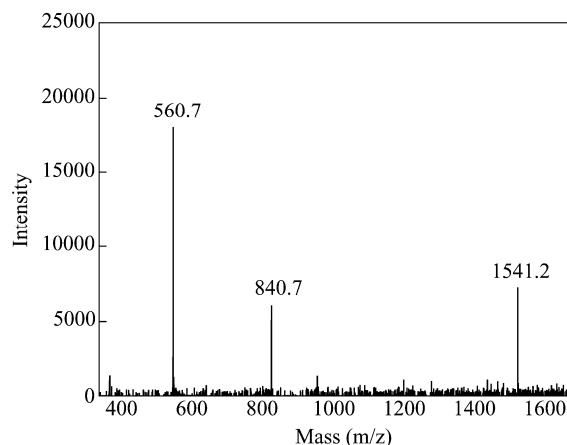


Fig. 9 Mass spectra of soluble PTAA film prepared from BFEE + 25% TFA (by volume) at a constant applied potential of 1.20 V
Solvent: H_2O

Thermal Analysis

Thermal degradation behavior of conducting polymers is very important for their potential applications. For most conducting polymers, the skeletal decomposition temperatures are generally reported to be lower than 600 K, which is not benefit for the applications. In order to investigate the thermal stability of PTAA film, the thermal analysis was tested as shown in Fig. 10(b). All thermal analyses were performed under a nitrogen stream in the temperature range 300–800 K with a heating rate of 10 K min^{-1} .

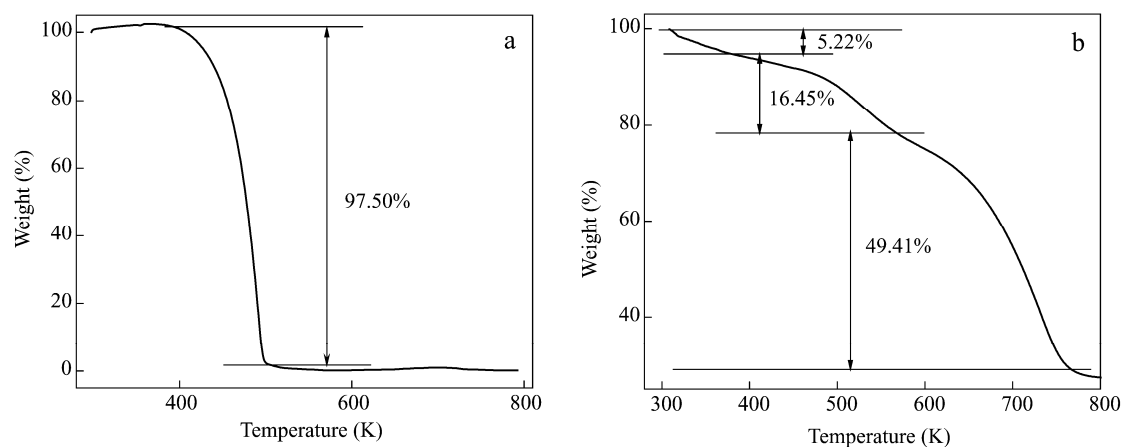


Fig. 10 TG curves of TAA (a) and dedoped PTAA film (b)
PTAA film was obtained potentiostatically at 1.2 V versus Pt from BFEE + 25% TFA.

From Fig. 10(b), it can be clearly observed that it was a three-step weight loss for PTAA. The polymer initially underwent a small weight decrease (about 5.22%) at relatively low temperature (from 300 K to 375 K), which may be attributed to water evaporation and other moisture trapped in the polymer. The weight loss was about 16.45% when the temperature reached 567 K. This degradation can be ascribed to a few of oligomers trapped in the polymer. With the gradual increasing of the temperature, a prominent weight loss step (about 49.41%) was clearly found at $637\text{ K} < T < 761\text{ K}$, which was essentially due to the oxidizing decomposition of the skeletal PTAA backbone chain structures. The maximal decomposition of the polymers appeared at 705 K. In addition, even when the temperature reached 800 K, the residual weight of the polymer films was 29.0%. The thermal property of TAA (Fig. 10a) was also investigated under the same conditions. In Fig. 10(a), when the temperature increased to about 393 K, a rapid weight loss process happened. The weight loss was about 97.50% when the temperature reached 500 K. These results indicate that the thermal stability of PTAA is better than TAA. Moreover, PTAA has higher thermal stability than most of the conducting polymers reported previously, such as poly(3-[4-(4-pentyl-cyclohexyl)-phenyl]-thiophene) (502 K)^[35], poly(3-methoxythiophene) (626 K)^[41], poly(9-aminofluorene) (395–551 K)^[42] and poly(9-hydroxyl-9-fluorene-carboxylic acid) (500–650 K)^[43]. Therefore, it can be concluded that the as-prepared PTAA film displays high decomposition temperatures, indicating that it can be applied in a wide temperature scale and suitable for some potential applications.

Conductivity and Morphology

The as-formed PTAA film can be peeled from the electrode into free-standing state (Fig. 11a). To the best of our knowledge, this is the first report on the electropolymerization of high quality of free-standing PTAA films. The size of the film can be controlled easily by controlling the size of the working electrode. Therefore, it can be expected that larger free-standing PTAA film can be obtained when larger working electrode is used. SEM image of doped PTAA film prepared in BFEE + 25% TFA is shown in Fig. 11(b). As can be seen from Fig. 11(b), PTAA film is flat and compact. The growth of the leaves is in the form of clusters. The coverage efficiency of the film is very high, without pinholes and cracks. However, after dedoping at a constant applied potential of 0.0 V, the surface of the PTAA film became uneven and disappearance of small particles (Fig. 11c). These differences between the doped and dedoped PTAA films were mainly due to the migration of counteranion out of the polymer film and the gradual solubility of oligomer from the electrode to the solution during the dedoping processes, which broke the smooth surface of the doped PTAA film.

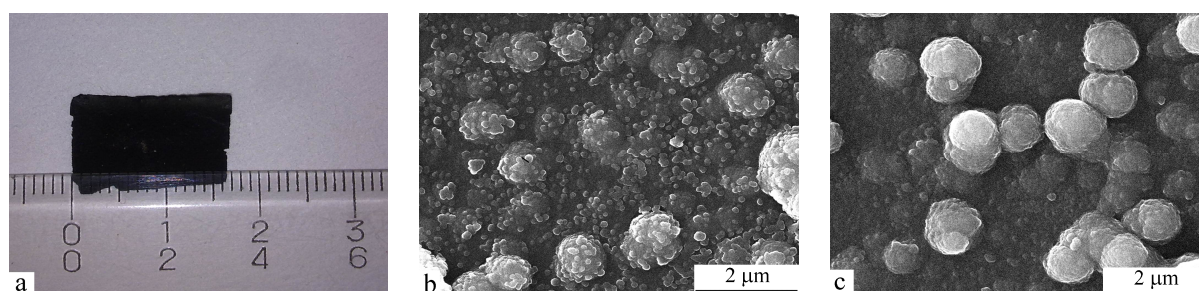


Fig. 11 (a) Photograph of the PTAA film and scanning electron microscopy images of doped PTAA (b) and dedoped PTAA (c) films

The conductivity of the doped PTAA film obtained from BFEE + 25% TFA was measured to be 7 S cm^{-1} , which was similar to the value of poly(3-(6-Bromohexyl)Thiophene) (20 S cm^{-1})^[40], higher than the value of poly(3-chlorothiophene) (0.1 S cm^{-1})^[27], poly(3-phenylthiophene) (0.01 S cm^{-1})^[44] and poly(3-methoxythiophene) (3.8 S cm^{-1})^[41]. Additionally, the electrical conductivity of dedoped PTAA film was measured to be 10^{-6} S cm^{-1} . These semiconducting properties will be useful in the applications of doped PTAA films. This good semiconducting property will facilitate their applications and, together with other excellent properties described above, will make PTAA very important in its use as active layers in light-emitting diodes^[45–47], which is one of the most promising applications of semiconducting conjugated polymers.

CONCLUSIONS

High quality water-soluble PTAA films with conductivity of 7 S cm^{-1} were electrochemically synthesized in BFEE + 25% TFA (by volume) by direct anodic oxidation of thiophene-3-acetic acid. The oxidation potential of TAA in this medium was determined to be only 0.37 V versus Pt, which was lower than that in ACN, 1.26 V versus Pt. The polymer film can be peeled from the electrode into free-standing state. According to FT-IR and $^1\text{H-NMR}$ spectra, the coupling between the monomer units mainly occurred at the C(2) and C(5) positions. TGA results indicated good thermal stability of PTAA films. The fluorescence spectra suggest that water-soluble PTAA is a good blue-light emitter. With these promising optical and electrical properties, PTAA may be a good candidate for the use as active layers in light-emitting diodes, one of the most important applications of semiconducting conjugated polymers.

REFERENCES

- 1 Briseno, A.L., Holcombe, T.W., Boukai, A.I., Garnett, E.C., Shelton, S.W., Frechet, J.J.M. and Yang, P.D., *Nano. Lett.*, 2010, 10: 334
- 2 Park, S.J., Kang, S.G., Fryd, M., Saven, J.G. and Park, S.J., *J. Am. Chem. Soc.*, 2010, 132: 9931
- 3 Liu, P., Wu, Y.L., Pan, H.L., Ong, B.S. and Zhu, S.P., *Macromolecules.*, 2010, 43: 6368
- 4 Pu, K.Y. and Liu, B., *J. Phys. Chem. B*, 2010, 114: 3077
- 5 Kim, D.M., Noh, H.B., Park, D.S., Ryu, S.H., Koo, J.S. and Shim, Y.B., *Biosens. Bioelectron.*, 2009, 25: 456
- 6 Piro, B., Do, V.A., Le, L.A., Hedayatullah, M. and Pham, M.C., *J. Electroanal. Chem.*, 2000, 486: 133
- 7 Constantine, C.A., Mello, S.V., Dupont, A., Cao, X.H., Jr, D.S., Jr, O.N.O., Strixino, F.T., Pereira, E.C., Cheng, T.C., Defrank, J.J. and Leblanc, R.M., *J. Am. Chem. Soc.*, 2003, 125: 1805
- 8 Eeg, F.S., Lindgren, M., Nilsson, K.P.R., Inganas, O. and Hammarstrom, P., *Chem. Phys.*, 2007, 336: 121
- 9 Chan, H.S.O., Toh, C.S. and Gan, L.M., *J. Mater. Chem.*, 1995, 5: 631
- 10 Ryder, K.S., Morris, D.G. and Cooper, J.M., *Biosens. Bioelectron.*, 1997, 12: 721
- 11 Vaddiraju, S., Seneca, K. and Gleason, K.K., *Adv. Funct. Mater.*, 2008, 18: 1929
- 12 Gigliotti, M., Strixino, F.T., Matsushima, J.T., Bulhoses, L.O.S. and Pereira, E.C., *Sol. Energ. Mat. Sol. C*, 2004, 82: 413
- 13 Okutan, M., Yerli, Y., San, S.E., Yilmaz, F., Gunaydin, O. and Durak, M., *Synthetic. Met.*, 2007, 157: 368
- 14 Hara, K., Sayama, K. and Arakawa, H., *Bull. Chem. Soc. Jpn.*, 2000, 73: 583
- 15 Malitesta, C., Guascito, M.R., Mazzotta, E. and Picca, R.A., *Thin Solid Films*, 2010, 518: 3705
- 16 Xu, J.K., Shi, G.Q., Xu, Z.J., Chen, F.E. and Hong, X.Y., *J. Electroanal. Chem.*, 2001, 514: 16
- 17 Lu, B.Y., Yan, J., Xu, J.K., Zhou, S.Y. and Hu, X.J., *Macromolecules*, 2010, 43: 4599
- 18 Lu, B.Y., Xu, J.K., Fan, C.L., Jiang, F.X. and Miao, H.M., *Electrochim. Acta*, 2008, 54: 334
- 19 Lu, B.Y., Xu, J.K., Li, Y.Z., Liu, C.C., Yue, R.R. and Sun, X.X., *Electrochim. Acta*, 2010, 55: 2391
- 20 Lu, B.Y., Liu, C.C., Li, Y.Z., Xu, J.K. and Liu, G.D., *Synthetic. Met.*, 2011, 161: 188
- 21 Inagi, S., Yamaguchi, T., Hayashi, S., Koseki, K. and Fuchigami, T., *Electrochem. Commun.*, 2010, 12, 661
- 22 Nie, G.M., Guo, Q.F., Zhang, Y. and Zhang, S.S., *Eur. Polym. J.*, 2009, 45: 2600
- 23 Nie, G.M., Cai, T., Xu, J.K. and Zhang, S.S., *Electrochem. Commun.*, 2008, 10: 186
- 24 Xu, J.K., Zhou, W.Q., Chen, B., Pu, S.Z., Wang, J.W. and Wan, Y.Q., *J. Polym. Sci. Polym. Chem.*, 2006, 44: 1125
- 25 Xu, J.K., Shi, G.Q., Zhang, J.X. and Hong, X.Y., *Macromol. Chem. Phys.*, 2002, 203: 2385
- 26 Xu, J.K., Zhou, W.Q., Hou, J., Pu, S.Z., Wei, Z.H. and Wang, J.W., *Mater. Lett.*, 2006, 60: 2569
- 27 Xu, J.K., Shi, G.Q., Xu, Z.J., Chen, F.E. and Hong, X.Y., *J. Electroanal. Chem.*, 2001, 514: 16
- 28 Lu, B.Y., Li, Y.Z. and Xu, J.K., *J. Electroanal. Chem.*, 2010, 643: 67
- 29 Nie, G.M., Cai, T., Qu, L.Y., Xu, J.K., Wei, Q.L. and Zhang, S.S., *J. Electroanal. Chem.*, 2008, 612: 191
- 30 Li, Chun., Chen, F.E., Shi, G.Q., Xu, J.K. and Xu, Z.J., *J. Appl. Polym. Sci.*, 2002, 83: 2462
- 31 Lu, B.Y., Zeng, L.Q., Xu, J.K., Le, Z.G. and Rao, H.Y., *Eur. Polym. J.*, 2009, 45: 2279

- 32 Lu, B.Y., Li, Y.Z. and Xu, J.K., *J. Electroanal. Chem.*, 2010, 643: 67
- 33 Xu, J.K., Shi, G.Q., Zhang, J.X. and Hong, X.Y., *Macromol. Chem. Phys.*, 2002, 203: 2385
- 34 Lu, B.Y., Xu, J.K., Fan, C.L., Miao, H.M. and Shen, L., *J. Phys. Chem. B*, 2009, 113: 37
- 35 Zhang, Z., Tang, H., Liang, X. and Shi, G.Q., *J. Electroanal. Chem.*, 2006, 587: 308
- 36 Fan, C.L., Xu, J.K., Chen, W. and Dong, B., *J. Phys. Chem. C*, 2008, 112: 12012
- 37 Dong, B., Xing, Y.H., Xu, J.K., Zheng, L.Q., Hou, J. and Zhao, F., *Electrochim. Acta*, 2008, 53: 5745
- 38 Tsai, F.C., Chang, C.C., Liu, C.L., Chen, W.C. and Jenekhe, S.A., *Macromolecules*, 2005, 38: 1958
- 39 Nie, G.M., Han, X.J., Hou, J. and Zhang, S.S., *J. Electroanal. Chem.*, 2007, 604: 12
- 40 Xu, J.K., Wei, Z.H., Du, Y.K., Pu, S.Z., Hou, J. and Zhou, W.Q., *J. Appl. Polym. Sci.*, 2008, 109: 1570
- 41 Dong, B., Xu, J.K., Zheng, L.Q. and Hou, J., *J. Electroanal. Chem.*, 2009, 628: 60
- 42 Fan, C.L., Xu, J.K., Chen, W. and Dong, B., *J. Phys. Chem. C*, 2008, 112: 12012
- 43 Fan, C.L., Xu, J.K., Chen, W., Lu, B.Y., Miao, H.M., Liu, C.C. and Liu, G.D., *J. Phys. Chem. C*, 2009, 113: 9900
- 44 Zhang, Z.P. and Shi, G.Q., *J. Electroanal. Chem.*, 2004, 569: 197
- 45 Zhu, Z.J., Li, Y.Z., Pei, M.S., Xu, J.K., Lu, B.Y. and Shen, L., *Acta Polymerica Sinica (in Chinese)*, 2010, (6): 714
- 46 Wang, J., Miao, H.M., Lu, B.Y., Xu, J.K., Li, Y.Z. and Zhang, H.L., *Acta Polymerica Sinica (in Chinese)*, 2011, (3): 327
- 47 Yue, R.R., Xu, J.K., Lu, B.Y., Liu, C.C., Zhu, Z.J. and Zhang, Z., *Chinese. J. Polym. Sci.*, 2010, 28(5): 771