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Electrochemical and spectroscopic characteristics of copolymers electrochemically synthesized from 3-(4-fluorophenyl)thiophene and 3,4-ethylenedioxythiophene

ZHENHONG WEI, JINGKUN XU*, JIAN HOU, WEIQIANG ZHOU, SHOUZHI PU
Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China
E-mail: xujingkun@tsinghua.org.cn or xujingkun@mail.ipc.ac.cn

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The copolymerization of 3-(4-fluorophenyl)thiophene (FPT) and 3,4-ethylenedioxythiophene (EDOT) was successfully achieved electrochemically in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte by direct anodic oxidation of the monomer mixtures on platinum or stainless steel electrodes. As-formed copolymer own both the advantages of poly(3-(4-fluorophenyl)thiophene) (PFPT) and poly(3,4-ethylenedioxythiophene) (PEDOT), such as good electrochemical behaviors, high conductivity and excellent ambient stability. The structure and morphology of the copolymer were investigated by UV-vis, infrared spectroscopy, thermal analysis and scanning electron microscopy (SEM), respectively. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

In the past 25 years, inherently conducting polymers, such as poly (para-phenylene), polyaniline, polypyrrole, etc., have attracted great attention due to their wide fundamental interest and potential application. Among them, polythiophenes have the advantages of good electrical conductivity and ease of anodic electrodeposition of free-standing films and can be good candidates for applications in various domains like electronics, electrocatalysis and pharmacology. Until now, a large number of substituted thiophene derivatives have been obtained, resulting in numerous polymers with different degrees of stability, conductivity, solubility and bandgap [1–6]. For example, poly (3-(4-fluorophenyl)thiophene) (PFPT) has a potential application in type III supercapacitors with improved both *p*-doping and n-doping performance [7–14]. The substitution of fluorophenyl group on β-position of thiophene can improve the thermal stability of corresponding polymer. However, steric effect of this group makes the electrodeposition of high quality films very difficult although the monomer is very cheap and the corresponding polymer can be easily produced one step in large scale. This also leads to relatively low electrical conductivity of PFPT films. On the other hand, poly (3,4-ethylenedioxythiophene) (PEDOT) is useful as an antistatic coating and potential electrochromic material with two electron-donating oxygen atoms adjacent to the thiophene ring stabilizing the positive charges generated in doped PEDOT and lowering the relative bandgap. It also shows a dramatic shift of redox potential to the cathodic range with good environmental stable conductivity as high as 10^2 S/cm [15–25]. Generally, simple thiophene and its derivatives usually have high oxidation potentials, which results in the irreversible over-oxidation of the polymer deposited on the electrode. Consequently, polythiophene films deposited from the common electrochemical solvents are of low quality and poorly conducting. This is so-called polythiophene paradox. Because of the electron-donating group-*O*-substitution, the oxidation potential of EDOT is greatly lowered. Therefore, high quality PEDOT films can be easily produced and the polythiophene paradox can be solved. Based on its excellent properties, PEDOT was widely investigated for application such as in type III capacitor. However, the preparation of EDOT monomer is very complex and expensive. For modern and industrial purpose, it is very eager to get the polymer with excellent properties together with low cost for their preparation.

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[*] Author to whom all correspondence should be addressed.

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Recently, much interest has been focused on the copolymerization in order to prepare conducting polymers with better properties to overcome the limitation of the rarity of new monomers. So far, copolymers of funan with pyrrole [26], funan with 3-methyl thiophene [27], pyrrole with indole [28–30], EDOT with pyrrole [31, 32], EDOT with indole [33], 3-methylthiophene with 3-chlorothiophene [34], etc., have been prepared successfully by direct electrochemical oxidation of mixtures of the corresponding monomers. Several new conducting polymers show obvious advantages, such as variation of conductivity, enhancement of electrochemical activity and thermal stability. The successful copolymerization can be assigned to the fact that the oxidation potential onsets of the corresponding monomers are close to each other. However, to the best of our knowledge, electrochemical copolymerization of 3-(4-fluorophenyl)thiophene (FPT) with 3,4-ethylenedioxythiophene (EDOT) has not been reported yet. It is expected that copolymerization of FPT and EDOT might combine their properties and produce new properties intermediate between PFPT and PEDOT, which may be greatly helpful in the electronic materials in type III capacitors.

In this paper, FPT and EDOT were copolymerized successfully by electrochemical oxidation of the monomer mixtures. The electrochemistry of PFPT, PEDOT and copolymers of FPT with EDOT were studied. In addition, the thermal stability, spectroscopic properties, morphology and conductivity of as-formed copolymer films were investigated in detail.

2. Experimental

2.1. Materials

3-(4-Fluorophenyl)thiophene (FPT) was synthesized by a coupling reaction of 3-bromothiophene and 4-fluorophenylmagnesium bromide in THF using $NiCl_2$ (diphenylphosphino propane) as catalyst and purified by sublimation as illustrated in Scheme 1 [35–37]. 3,4-ethylenedioxythiophene (EDOT, Aldrich) was used as received without further purification. Tetrabutylammonium tetrafluoroborate (TBATFB, Acros Organics, 95%) was dried in vacuum at 60°C for 24 h before use. Commercial HPLC grade acetonitrile (ACN, made by Shanghai Chemical Reagent Company) was dried and distilled before use.

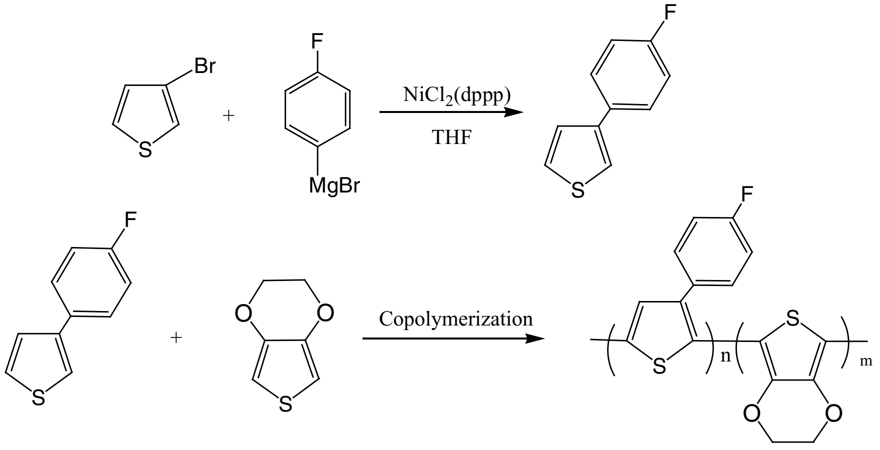
2.2. Electrochemical experiments

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. The working and counter electrodes for cyclic voltammetric experiments were platinum wire and stainless steel wire with a diameter of 0.5 mm and 1 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^2 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. A platinum wire with a diameter of 0.5 mm was used as the quasi-reference electrode. It is calibrated using the ferrocene (Fc/Fc^+) redox couple which has a formal potential of $E_{1/2} = +0.35$ V versus platinum wire in this medium. The polymers were deposited on an indium-tin-oxide (ITO) coated glass for UV-visible spectral measurements. The thickness of these films was controlled by the deposition time according to Equation 1 [38]:

$$d = IT(65 + yM)/(2 + y)FD \qquad (1)$$

where I is the current density, T is the deposition time, y is the doping level of the polymer (generally 0.3), M is the molar mass of the doping anions, F is the Faraday constant (96500 C mol^{-1}), D is the density of the polymer film (here is estimated to be 1.2 g cm^{-3}).

All the samples were grown in an ACN solution containing 0.1 M TBATFB as a supporting electrolyte. All



Scheme 1 The synthesis route of FPT monomer and its electrochemical copolymerization with EDOT.

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. In order to remove the electrolyte and 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.

2.3. Characterizations

The conductivity of polymer films was measured by conventional four-probe technique. UV-visible spectra were taken by using Perkin Elmer Lambda 900 UV-vis-NIR spectrophotometer. Infrared spectra were recorded using Bruker Vertex 70 FT-IR spectrometer with KBr pellets. The thermogravimetric (TG) analysis was performed with a thermal analyzer of NETZSCH TG209. Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6700F scanning electron microscopy.

3. Results and discussion

3.1. Electrochemical copolymerization

To determine the proper conditions for electropolymerization in ACN + 0.1 M TBATFB system, the anodic oxidation of FPT and EDOT monomers were examined. The onset of EDOT polymerization was at 1.06 V (Fig. 1A), and that for FPT was at 1.28 V (Fig. 1E). The small distinction (0.12 V) between the oxidation onsets of the two monomers implied that the copolymerization of FPT and EDOT is feasible. To identify proper stoichiometries for copolymer formation, copolymers were formed from various feed ratios at a fixed concentration of 0.05 M FPT. When the feed ratio of EDOT/FPT was 0.05:0.05, the initial oxidation onset of the copolymer was at 1.12 V (Fig. 1B). When the feed ratios of EDOT/FPT were 0.025:0.05 and 0.0177:0.05, the oxidation onsets of the copolymer were at 1.15 V and 1.22 V, respectively (Fig. 1C and D). With the concentration decreases of EDOT, the oxidation potential onsets of the copolymer shifted positively. The oxidation potentials of the mixture of FPT and EDOT were between that of the two monomers suggested the two monomers can be oxidized alternately and the copolymer chains were composed of alternate FPT and EDOT units.

The successive cyclic voltammograms (CVs) of FPT, EDOT and the mixture of the two monomers in ACN containing 0.1 M TBATFB at potential scanning rates of 100 mV/s were illustrated in Fig. 2. The electrochemical polymerizations of FPT and EDOT in ACN solution both showed characteristics of electrosyntheses of common conducting polymers, such as polypyrrole and polythiophene derivatives. As the CV scan continues, conducting polymer films were also formed on the working electrode surface. The increase in the redox wave currents implied that the amount of the polymer on the electrode was increasing. PFPT polymer can be reduced and oxidized between 0.74 and 0.89 V (Fig. 2A). Similar to the literature, the CVs of EDOT showed broad redox waves and PEDOT polymer can be reduced and oxidized between −0.6 and 0 V (Fig. 2B). When the CVs were taken in the electrolytic solutions containing the mixture EDOT/FPT = 0.05:0.05 and 0.025:0.05, great differences in the CVs can be easily observed (Fig. 2C and D). In sharp contrast to pure FPT, the oxidation and reduction potentials of the mixture both shifted negatively. The evolution of a new wave at a potential different from the potentials of both pure FPT and EDOT suggested the formation of a copolymer. When the concentration of EDOT was reduced from 0.05 M to 0.025 M, the redox peak values of the copolymers shifted from −0.1 V and 0.4 V (Fig. 2C) to 0.25 V and 0.6 V(Fig. 2D). This implied that more FPT units were incorporated into the copolymer film when the concentration of EDOT was reduced.

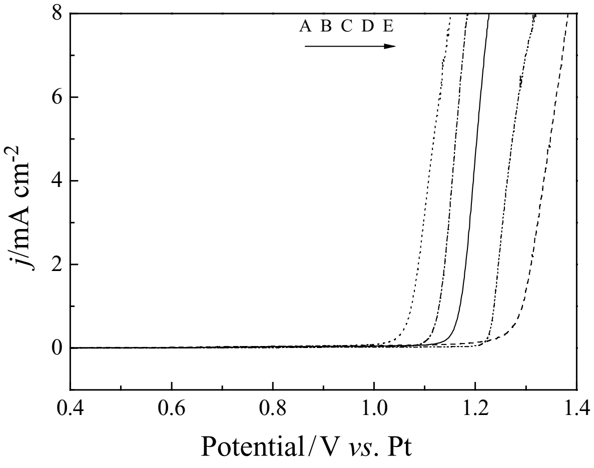


Figure 1 Anodic polarization curves of 0.05 M EDOT (A), 0.05 M EDOT + 0.05 M FPT (B), 0.025 M EDOT + 0.05 M FPT (C), 0.0177 M EDOT + 0.05 M FPT (D) and 0.05 M FPT in ACN + 0.1 M TBATFB (E). Scanning rates: 20 mV/s.

3.2. Electrochemistry of copolymer films

Based on the above observation, further studies were carried out for PFPT, PEDOT films and above copolymer films. The electrochemical properties of these polymer films were characterized by CVs in monomer-free ACN + 0.1 M TBATFB solution. The CVs of PFPT, PEDOT and copolymers with two different concentrations of EDOT monomer were given in Fig. 3A–D, respectively. Similar to the results of substituted polythiophenes, the steady-state cyclic voltammograms represented broad anodic and cathodic peak. The currents were proportional to the scan rates (Fig. 3 insert), indicating a redox couple fixed on the electrode. Furthermore, these films can be cycled repeatedly between the conducting and insulating state with no significant decomposition. As can be seen from Table I PFPT can be oxidized and reduced from 1.12 V to 0.88 V. For PEDOT, much lower potentials were needed to oxidize or reduce the film (from 0.25 V to −0.68 V).

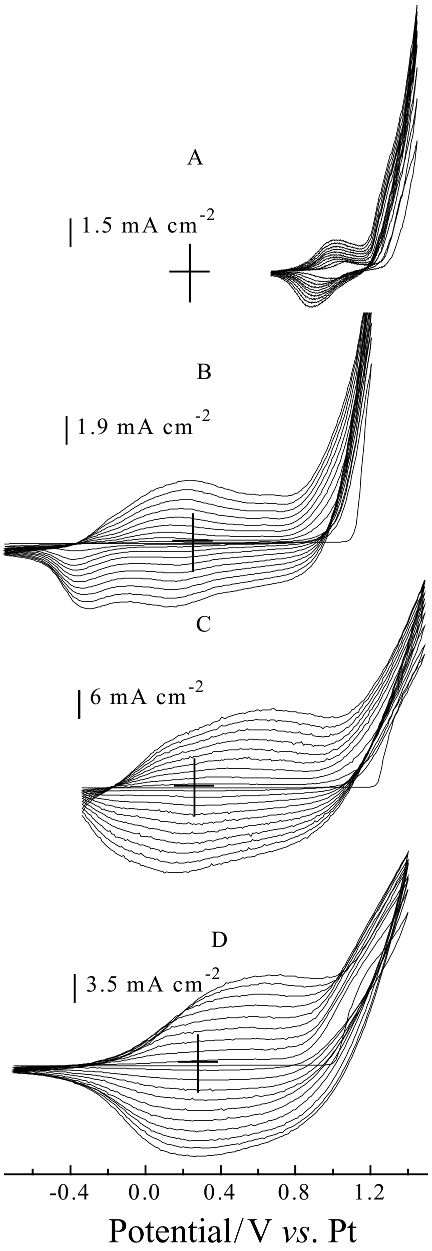


Figure 2 Cyclic voltammograms of 0.05 M FPT (A), 0.05 M EDOT (B), 0.05 M EDOT + 0.05 M FPT (C) and 0.025 M EDOT + 0.05 M FPT in ACN + 0.1 M TBATFB (D). Scanning rates: 100 mV/s.

On the other hand, the CVs of copolymer film prepared from mixture of EDOT and FPT had a new pair of anodic and catholic peaks. When the feed ratio of FPT/EDOT was 0.05:0.05, the copolymer showed a couple of redox waves at 0.32 V and 0.059 V, close to the values of EDOT. When the feed ratio became 0.05:0.025, the redox peaks located at around 0.25 V and –0.01 V. The redox potentials of copolymers changed slightly with the decrease of EDOT concentration. These indicated that the EDOT monomer had dominant effect on the copolymer composition and its electrochemical characteristics. If the concentration of EDOT was equal to FPT, EDOT sequences dominated in the copolymer structure. If the concentration of EDOT/FPT = 1:2, FPT sequences dominated in the copolymer structure. Furthermore, the other two mixed films were prepared for comparison. The one film was obtained by initially deposited in the solution of 0.05 M FPT at the constant potential 1.4 V for 40 s, then deposited in the solution of 0.05 M EDOT at a constant applied potential of 1.2 V for the same time. The other film was prepared by reverse order in the FPT and EDOT solution for the same 40 s. These two films were also cycled in the solution of ACN + 0.1 M TBATFB as shown in Fig. 3E and F. The figures of these two mixed films were similar to that of PEDOT, which indicated that the electrochemical properties of PEDOT were more active than that of PFPT. So, in order to successfully obtain the copolymer, the concentration of EDOT and FPT should be carefully controlled.

It is well known that PEDOT can be used as stable conducting materials in tantalum capacitors owing to its pretty good redox properties [39, 40]. According to Fig. 3B it is obvious that there was a distinct capacitive feature of the charge storage. A rapid increase in current density followed by a plateau occurred during the process of potential scan, while the reverse course showed the discharge of the stored charge as the capacitor returned to its original state. On the other hand, PFPT also can be used as a very important capacitor, but its electrochemical activity and capacitive property are much lower than that of PEDOT. The values of cathodic and anodic current density of PEDOT were −15 and 19 mA/cm^2, much higher than those of PFPT (−5.6 and 6 mA/cm^2) as shown in Table I. When the copolymer was prepared from mixture of 0.05 M FPT and 0.05 M EDOT, the electrochemical behaviors were similar to that of PFPT with the cathodic and anodic current density of −6.5 and 7 mA/cm^2. If the copolymer was prepared from the feed ratio of 0.05:0.025, the copolymer waves showed significant greater redox activity compared with pure PFPT. The values of cathodic and anodic current density were −9.4 and 10.7 mA/cm^2. These results indicated that the copolymer has improved the electrochemical activity and capacitive property of pure PFPT by incorporating EDOT units into the copolymer.

3.3. Structural characterizations

According to the method of Kuwabata *et al.* [41], the concentrations of EDOT and FPT for large amount copolymer production were chosen as 0.05 M and 0.025 M. During the potentiostatistic process, the color of solutions around the electrode darkened progressively. With the polymerizing propagation, part soluble oligomers became insoluble and deposit on the working electrode with the elongation of the polymer main chain. However, there were still part oligomers, which diffused from the electrode into the bulk solution. PFPT film was very difficult to deposit on stainless steel sheets. They can be obtained from the solution by filtration, which was dark red powder in doped state and insoluble in organic solvents. PEDOT film changed its color from transparent pale blue in doped state to opaque dark blue in dedoped form, and cannot dissolve in organic solvents either. For the copolymers, their colors changed from dark green in doped state to brown in dedoped state, also insoluble in all organic solvents.

The UV-visible spectra of the pure PFPT, PEDOT and the copolymer films prepared potentistatically from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT on ITO coated glass were shown in Fig. 4 respectively. The spectrum of the PFPT film showed a characteristic absorption at about 375 nm and 525 nm (Fig. 5A). On the other hand, the spectrum of the PEDOT films showed a narrow absorption at 360 nm and a much broader absorption from 500 nm to about 800 nm (Fig. 5B). The spectrum of copolymer showed characteristic absorptions at 430 nm, which was a red shift in contrast to pure PFPT due to the incorporation unit of EDOT, further confirming the occurrence of copolymerization.

PEDOT, PFPT and copolymers prepared potentiostatically from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT were also analyzed by

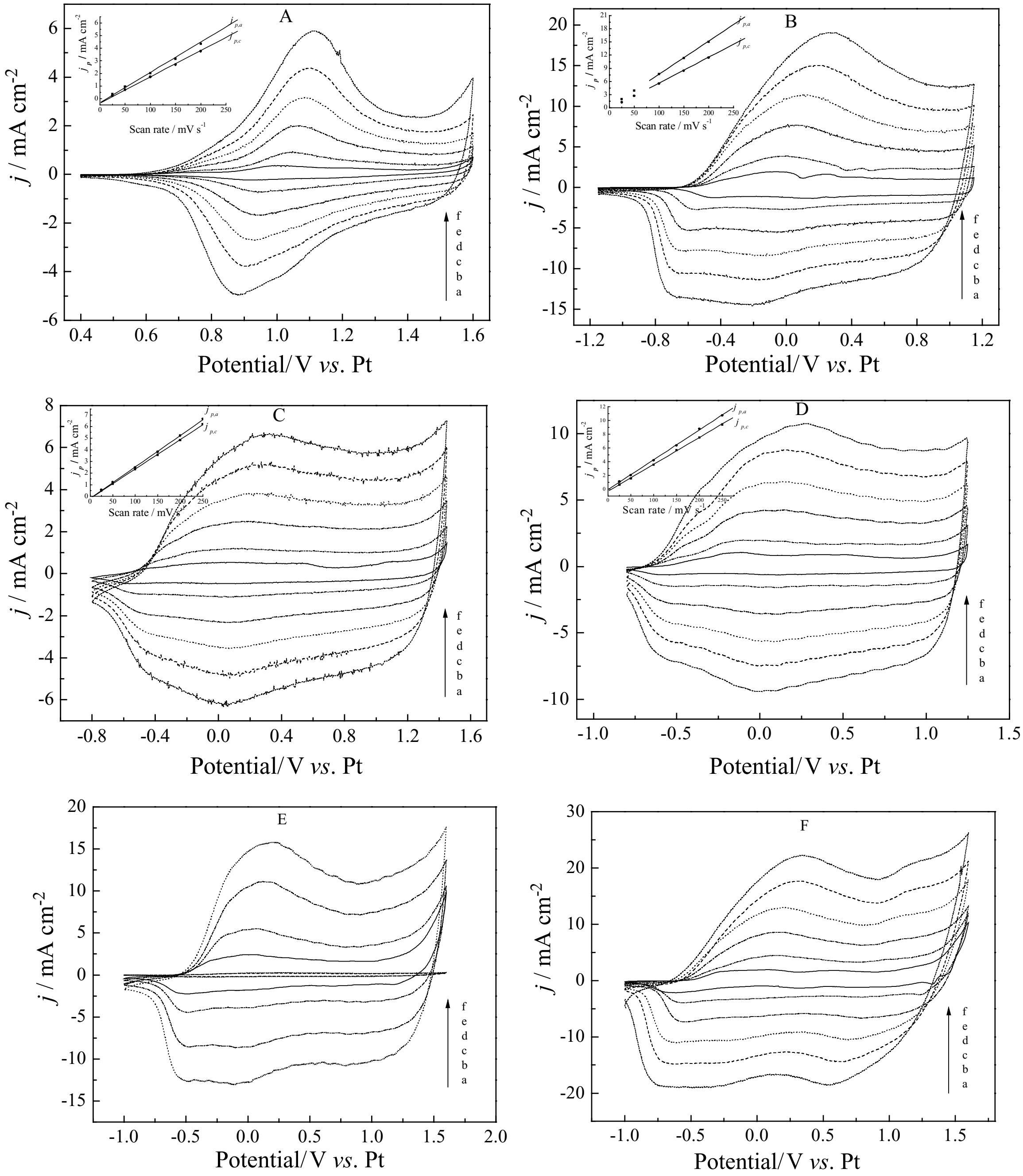


Figure 3 Cyclic voltammograms of PFPT film (A), PEDOT film (B), poly(EDOT-co-FPT = 1:1) (C), poly(EDOT-co-FPT = 1:2) film (D) and two mixed films (E), (F) recorded in ACN + 0.1 M TBATFB at potential scan rates of 250 mV/s (a), 200 mV/s (b), 150 mV/s (c), 100 mV/s (d), 50 mV/s (e), 25 mV/s (f). The polymer films (A, B, C, and D) were electrochemically synthesized at constant applied potentials of 1.38 V, 1.16 V, 1.24 V and 1.28 V, respectively. The mixed film (E) was electrochemically synthesized by turn in the solutions of 0.05 M FPT and 0.05 M EDOT at the constant potentials of 1.38 V and 1.16 V. The mixed film (F) was obtained according to the reverse order compared to film E.

TABLE I The redox peak values and capacities of PFPT, PEDOT and copolymers prepared at constant applied potentials of 1.38 V, 1.16 V and 1.28 V respectively. The copolymer were prepared from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT

	Oxidation		Reduction	
	Potential (V)	Capacity (mA/cm^2)	Potential (V)	Capacity (mA/cm^2)
Pure PFPT	1.12	6	0.88	−5.8
Pure PEDOT	0.25	19	−0.68	−15
Poly(EDOT/FPT = 1:1)	0.32	7	0.059	−6.5
Poly(EDOT/FPT = 1:2)	0.28	10.7	−0.01	−9.4

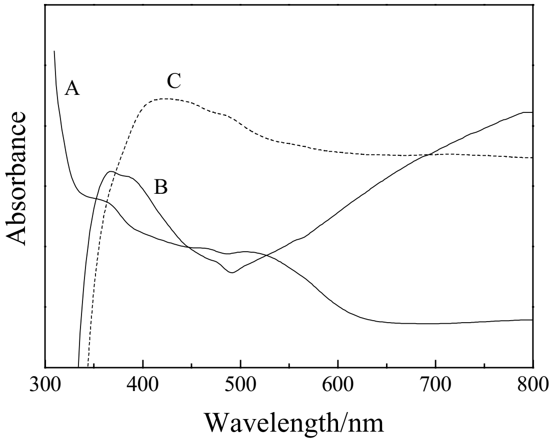


Figure 4 UV-vis spectra of the PFPT (A), PEDOT (B) and copolymer film (C)coated on an optically transparent ITO electrode at 1.38 V, 1.16 V and 1.28 V, respectively. The thickness of PFPT, PEDOT and copolymer were 0.27 μm, 0.53 μm and 0.36 μm respectively. The copolymer films were prepared from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT.

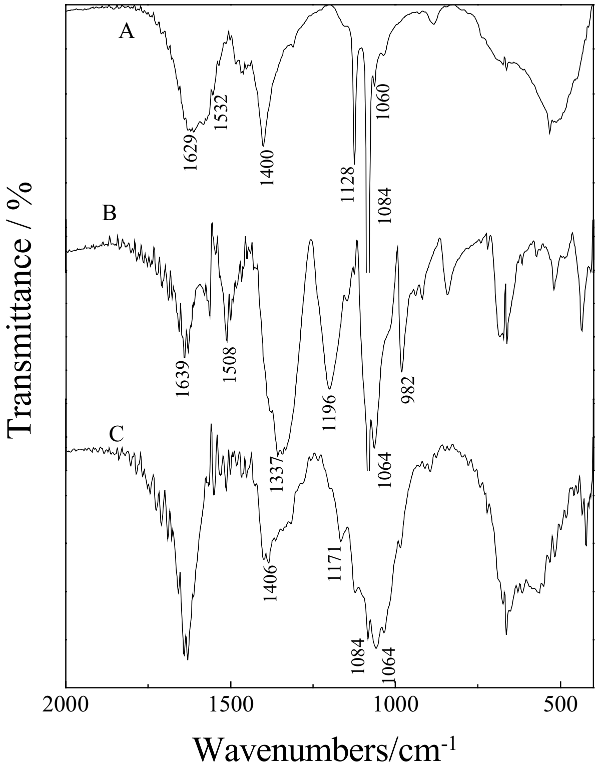


Figure 5 Infrared spectra of pure PFPT (A), purePEDOT (B) and copolymer (C) prepared at 1.38 V, 1.16 V and 1.28 V, respectively. The copolymer were prepared from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT.

FT-IR spectroscopy, as shown in Fig. 5. According to the spectrum of PFPT (Fig. 5A), the absorption at 840 cm^{-1} indicated the existence of a 1,4-disubstituted benzene ring and the benzene was very stable during the polymerization process. The C-F vibrations were located at 1400 cm^{-1}. The bands at 1629 cm^{-1}, 1532 cm^{-1}, 1501 cm^{-1} can be ascribed to the skeleton vibration of thiophene ring. The bands at 1128 cm^{-1}, 1084 cm^{-1} and 1060 cm^{-1} can be ascribed to the special skeleton vibration of halogen substituted benzene. According to the spectrum of pure PEDOT (Fig. 5B), the bands at 1639 cm^{-1}, 1508 cm^{-1}, 1337 cm^{-1} originated from the stretching modes of C=C and C–C in the thiophene ring. The bands at 1195 cm^{-1}, 1142 cm^{-1} and 1064 cm^{-1} were assigned to the stretching of the C–O–C bond. Furthermore, vibrations from the C–S bond in the thiophene ring of PEDOT were shown at 982 cm^{-1}. In the spectrum of the copolymer, the characteristic peaks of PFPT and PEDOT homopolymers can also be found in the copolymers (Fig. 5C). The bands at 1171 cm^{-1}, 1084 cm^{-1} and 1064 cm^{-1} were assigned to the stretching of the C–O–C bond in EDOT monomer, while the bands at 1406 cm^{-1} were belonged to the C–F vibration in FPT monomer. In order for better comparison, the band assignments were also list in Table II. All these features implied that copolymerization happened during the potentiostatic electropolymerization of EDOT and FPT, in consistent with the results of the cyclic voltammetry.

3.4. Thermal analysis

The degradation behaviors of conducting polymers are very important for their potential applications. Therefore, the thermal analysis of copolymer was tested by thermogravimetric analysis as shown in Fig. 6. All thermal analysis was performed under a nitrogen stream in the temperature range of 283–1000 K with a heating rate of 10 K/min. It can be seen from this figure, The PFPT film started to loss weight when the temperature reaches 523 K. The decomposition was up to 45% when the temperature reached 563 K. The bad thermal stability may be due to the short conjugated chain and poor PFPT film quality prepared from ACN (Fig. 6A). The PEDOT had a slight weight loss from 575 K to 603 K, up to 4.55% (Fig. 6B). This

TABLE II Band assignments of the infrared spectra of PFPT, PEDOT and poly(FPT-co-EDOT)

Assignments	PFPT (cm^{-1})	PEDOT (cm^{-1})	Poly(FPT-*co*-EDOT = 1:2) (cm^{-1})
1,4-substituted benzene	840		889
Thiophene ring vibration	1629	1639	1644
	1532	1508	1546
	1501	1337	1508
Halogen substituted benzene	1400		1406
	1128		1171
	1084		1122
C–O–C stretching vibration		1195	1084
		1142	1064
		1064	1029
C-S vibration	996	982	988

degradation can be ascribed to water evaporation or other moisture trapped in the polymer. The prominent decomposition of PEDOT happened at about 753 K (Fig. 6B). This weight loss was attributed to the degradation of the skeletal PEDOT backbone chain structure. The copolymer undergoes decomposition in several steps. The first weight loss occurred at about 553 K (Fig. 6C). This may be correlated to the decomposition of FPT unit. The second weight loss occurred at 593 K. This can be ascribed to the decomposition of EDOT unit. In addition, there was still evident decomposition about 35% between 623 K and 823 K, possibly due to the overflow of some oligmers that decomposed from the film with the increasing of temperature. For comparison, the degradation behaviors of equal quality of homopolymers were also tested. The mixture started to decomposition smoothly. The peak degradation occurred at about 555 K. This was the decomposition of both PFPT and PEDOT films. When the temperature reached 950 K, the mass loss was as high as 50.8%. The residual mass 49% was the sum of decomposed PFPT and PEDOT. The decomposition behavior of the blending two homopolymers was different to that of copolymer proved the occurrence of copolymerization.

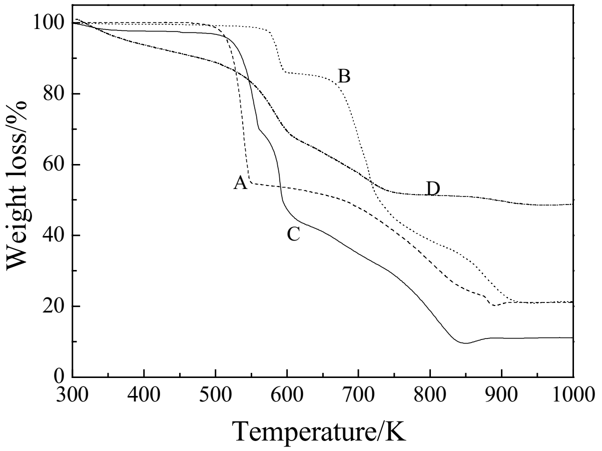


Figure 6 TGA curves of PFPT film (A), PEDOT film (B), poly(EDOT-co-FPT = 1:2) (C) and the equal quality mixtures of PFPT and PEDOT film (D). The copolymer were prepared from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT.

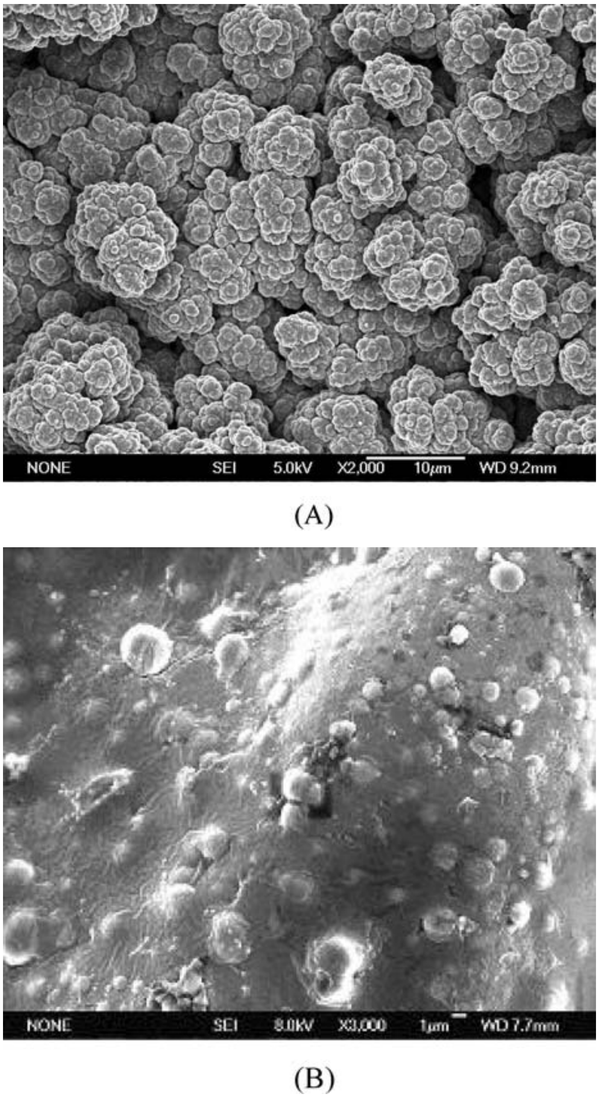


Figure 7 Scanning electron microscopy of PEDOT film (A) and a copolymer film (B) deposited on the electrode surface from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT.

3.5. Conductivity and morphology

The conductivities of PEDOT, PFPT and the copolymers obtained potentiostatically from ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT were recorded. Pure PEDOT exhibited excellent conductivity, up to 89 S/cm. On the contrary, the conductivity of PFPT was only about 0.1 S/cm. The conductivities of the copolymers were 2.5 S/cm between those of pure PEDOT and PFPT. This indicated that the insert of EDOT units into PFPT was helpful to improve the conductivity of PFPT, which may be beneficial to extend the applications of PFPT. On the other hand, the ease of FPT monomer preparation is also a good benefit for the application of PFPT-co-PEDOT copolymers in type III capacitors.

The properties of conducting polymers are strongly dependent on their morphology and structure. However, the quality of PFPT film obtained from ACN was poor, only little powder can be obtained on the electrode surface and most polymer films were dropped into the solution. Therefore, only the scanning electron micrographs (SEM) of PEDOT and copolymers were examined. As can be seen from Fig. 7A, PEDOT film was cauliflower-like. On the other hand, the copolymer is relatively compact and can be scraped off by a knife (Fig. 7B).

4. Conclusion

In this paper, electrochemical copolymerization of FPT and EDOT was successfully realized in ACN + 0.1 M TBATFB solution containing 0.05 M FPT and 0.025 M EDOT by the potentiostatic method. Incorporation of EDOT into PFPT chain allowed overcoming the limitations derived from the poor quality of PFPT obtained in ACN. The copolymers prepared from the mixtures show both the good properties of the FPT and EDOT monomers, such as good redox activity, capacitive property and electrical conductivity.

Acknowledgments

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