Electrodeposition of High Quality and Freestanding Poly(9,9-dioctylfluorene-*co*-thiophene) Films with Good Fluorescence Properties

Xingcong Wang,[1] Bing Chen,[1] Jingkun Xu,[1] Weiqiang Zhou,[2] Shouzhi Pu[1]

[1]*Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, China*
[2]*Institute of Coordination Catalysis, Yichun University, Yichun 336000, Jiangxi Province, China*

Received 26 April 2007; accepted 5 December 2007
DOI 10.1002/app.27872

ABSTRACT: The copolymerization of 9,9-dioctylfluorene (DOF) and thiophene (Th) was successfully achieved by direct anodic oxidation of monomer mixtures on platinum or stainless steel electrodes in boron trifluoride diethyl etherate (BFEE) containing additional 20% diethyl ether (by volume). The incorporation of Th units can produce high quality and freestanding poly(9,9-dioctylfluorene-*co*-thiophene) [poly(Th-*co*-DOF)] films with tunable fluorescence properties. As-formed copolymers were characterized by cyclic voltammetry, infrared, UV–visible, fluorescence spectroscopy, and thermal analysis. Copolymers films showed good electrochemical behavior and thermal stability. Fluorescence spectral studies indicated that the copolymer films have strong emissions from 390 to 500 nm, making them good candidates for application as blue–green light-emitting materials. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1924–1933, 2008

Key words: polyfluorenes; polythiophene; electrochemical copolymerization; boron trifluoride diethyl etherate; fluorescence properties; conducting polymers

INTRODUCTION

Polyfluorene (PF) and its derivatives (PFs) are one of the most wonderful candidate materials for application in polymer light-emitting diodes (PLEDs) because of their high fluorescence quantum yields, high hole mobility, good photostability, and stable blue light emission. In recent years, considerable efforts have been focused on the research of PFs, and the articles about PFs had a growth of a violent bombing.[1–5] C-9 position of fluorene with flexible alkyl chain can greatly improve the solubility of the resulting polymer.[5] However, the drawbacks of PFs, such as aggregation and excimer formation in solid state, and high energy barrier to hole injection, limited their application in PLEDs.[6–10]

Many approaches have been proposed to improve the performance of PFs, such as modification of the device structure by introducing an electron-transport layer,[11] blending,[12,13] copolymerization,[14,15] etc. However, copolymerization was one of the most important methods for improving the optical properties of individual polymers. The copolymerization of PFs at 2,7-positions with other monomers, which is widely used in the preparation of traditional copolymers, has also been employed to achieve specific electronic and/or physical properties of LEDs.[16–18]

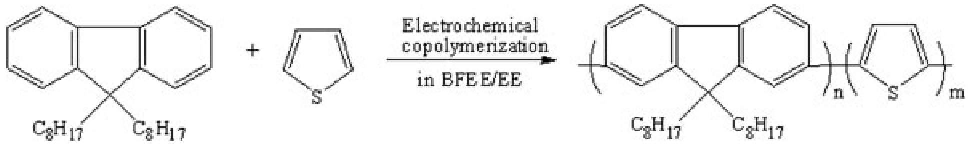
In previous studies, PFs and its copolymers were mainly prepared by chemical approaches such as Suzuki, Yamamoto, and Still couple reaction,[1–5] and little has been reported on electrochemical polymerization. In comparison with chemical approaches, which have disadvantages such as intricate processes, high costs, and low product yields, electrochemical polymerization has been proved to be one of the most useful approaches for conducting polymer (CP) synthesis, which has several distinct advantages such as catalyst-free, small amounts of monomer requirement, one-step conducting film formation, ease in control of the film thickness by the deposition charge, ease of characterization, etc.[19–22] Among CPs investigated during the past quarter century, polythiophene (PTh) was one of the most representative kind of materials for the copolymerization because of the advantages such as good environmentally stability, high conductivity, excellent mechanical properties, and high thermally stability.[19–22] According to the traditional view of electrocopolymerization, the success of copolymerization is mainly because of the closeness of the oxidation

---

Correspondence to: J. Xu (xujingkun@mail.ipc.ac.cn or xujingkun@tsinghua.org.cn).

Contract grant sponsor: Jiangxi Science and Technology Normal University, NSFC; contract grant number: 50663001.

Journal of Applied Polymer Science, Vol. 108, 1924–1933 (2008)



Scheme 1 The electrochemical copolymerization of DOF and thiophene in 80%BFEE + 20%EE solution.

potentials of the two monomers. The closeness of the oxidation potential of thiophene (Th) and 9,9-dioctylfluorene (DOF) implied the possibility of their electrochemical copolymerization, which would extend the applications of both poly(9,9-dioctylfluorene) (PDOF) and PTh.

On the other hand, the electropolymerization of Th needs a high oxidation potential above 1.6 V versus saturated calomel electrode (SCE) in common organic media such as acetonitrile, nitromethane, or propylene carbonate. The high oxidation potential would destroy the conjugation system because of overoxidation and lead to the poor quality of conducting films.[23] Boron trifluoride diethyl etherate (BFEE) was found to be a good electrolyte for electrochemical polymerization of aromatic compounds[24] such as pyrrole,[25,26] furan,[27,28] thiophene,[23,24,29–32] benzene,[32,33] naphthalene,[34,35] anthracene,[36] indole,[37–41] selenophene,[42,43] 3-(4-fluorophenyl)thiophene,[44] fluorine, and its derivatives,[45,46] etc. Utilizing BFEE, the oxidation potentials of aromatic monomers can be considerably lowered. High quality PTh and its derivatives films can be prepared in BFEE by direct anodic oxidation of corresponding monomers.[24] Meanwhile, the mechanical properties and flexibility of the CPs were greatly improved with the formation of long polymer chains. This unique property may facilitate the application of PThs. In our study, the electrochemical polymerization of DOF was also performed in BFEE.[46] Although the film quality of as-formed PDOF was greatly improved in comparison with those prepared in common organic solvents, they still cannot meet the quality requirement for their potential application.

According to the electrochemical copolymerization, many high quality copolymers have been prepared successfully by direct electrochemical polymerization from mixtures of different monomers in BFEE, such as copolymers of furan with pyrrole,[47] indole with pyrrole,[48] 3-methylthiophene (MeT) with 3-chlorothiophene,[49] furan with MeT,[50] 3-(4-fluorophenyl)thiophene with MeT,[51] 3-butylthiophene with 3-bromothiophene,[52] carbazole with MeT,[53] 3,4-ethylenedioxythiophene with indole,[54] fluorene with MeT,[55] etc. To the best of our knowledge, the electrochemical copolymerization of DOF with Th in BFEE has not been reported so far. On the basis of considerations mentioned earlier, it will be of great significance if a new polymer that owns the advantages of both PDOF and PTh can be electrodeposited.

In this article, DOF and Th were copolymerized successfully in BFEE + 20% diethyl ether (Scheme 1). The electrochemical, spectroscopic properties, thermal stability, conductivities, and morphology, especially the fluorescence properties of copolymer films were investigated in detail.

EXPERIMENTAL

Materials

Thiophene (Th) (Acros Organics, 99%, New Jersey) was used as received without further purification. 9,9-Dioctylfluorene (DOF) was synthesized as reported earlier.[56] Boron trifluoride diethyl etherate (BFEE, Beijing Changyang Chemical Plant, China) was distilled and stored at −20°C before use. Tetrabutylammonium tetrafluoroborate (Acros Organics, 95%, New Jersey) was dried in vacuum at 60°C for 24 h before use. Concentrated sulfuric acid (98%) and 25% ammonia were used as received without further purification. Diethyl ether (EE) was purified by fraction distillation over sodium/benzophenone and handled in a moisture-free atmosphere.

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, respectively. They were polished and cleaned by water and acetone successively before each examination. In the past investigations of the electrosyntheses of high quality PTh films,[29,32] stainless steel electrode was found to be a good substrate for the preparation of PTh films and it can be easily peeled off the electrode. However, the PTh films were very hard to be peeled off Pt electrode under similar conditions. In addition, the stainless steel electrode also has other advantages such as cheapness and suitable for large-amount production. Therefore, 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 electro-

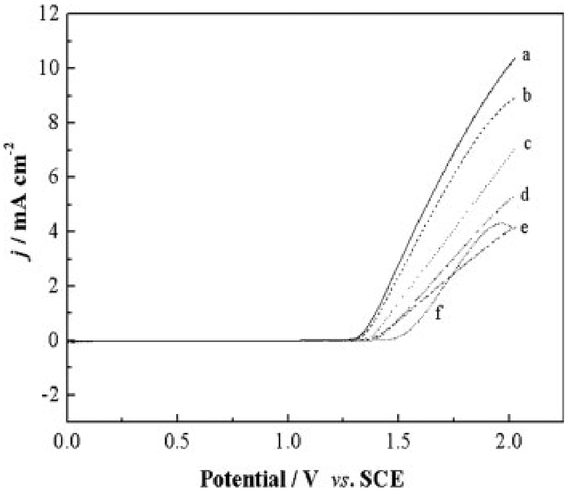


Figure 1 Anodic polarization curves of 0.05*M* Th (a), 0.0417*M* Th + 0.0083*M* DOF (b), 0.0375*M* Th + 0.0125*M* DOF (c), 0.033*M* Th + 0.017*M* DOF (d), 0.025*M* Th + 0.025*M* DOF (e), 0.05*M* DOF, and (f) in 80% BFEE + 20% EE solution. Potential scanning rates: 100 mV s^{-1}.

des, respectively. Stainless steel electrodes were carefully polished with abrasive paper (1500 mesh), and subsequently cleaned by water and acetone before each examination. The polymer and copolymer films used in various characterizations were deposited by using a potentiostatic technique except special notice. The copolymers were deposited on an indium-tin-oxide (ITO) coated glass for UV–visible and fluorescence spectral measurements. The neutral states were prepared by dedoping the polymer films at −0.2 V to exclude the dopant. All potentials were referred to a SCE.

The solubility of DOF in pure BFEE is not very good, while it is apt to dissolve in EE. Therefore, BFEE + 20% EE was chosen. All solutions were dearated 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 film was treated with 25% ammonia for 3 days, and then washed by water and acetone successively. After that, the polymer film was dried under vacuum at 60°C for 2 days.

Characterizations

Direct current electrical conductivity of as-formed polymer and copolymer 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. Fluorescence spectra were determined with Hitachi F-4500 fluorescence spectrophotometer. The thermogravimetric (TG) analysis was performed with a thermal analyzer of NETZSCH TG209.

RESULTS AND DISCUSSION

Electrochemical copolymerization

To determine the proper condition for electrochemical copolymerization in BFEE + 20% EE system, the anodic oxidation of DOF and Th with different molar ratios were examined. The oxidation potential onset of Th was at 1.32 V (vs. SCE) [Fig. 1(a)], while that for DOF was at 1.51 V [Fig. 1(f)]. The small distinction (0.19 V) between the oxidation onsets of

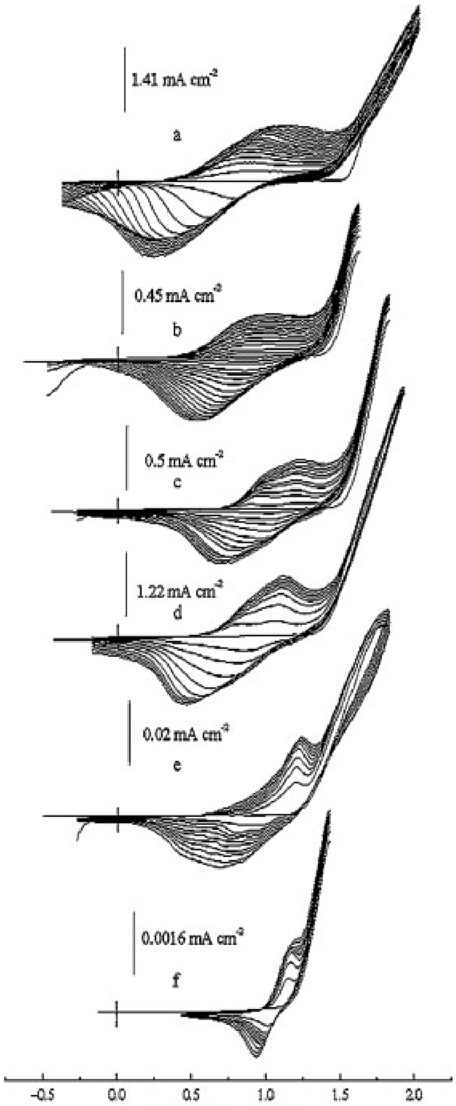


Figure 2 CVs of 0.05*M* Th (a), 0.0417*M* Th + 0.0083*M* DOF (b), 0.0375*M* Th + 0.0125*M* DOF (c), 0.033*M* Th + 0.017*M* DOF (d), 0.025*M* Th + 0.025*M* DOF (e), 0.05*M* DOF (f) in 80% BFEE + 20% EE solution. Potential scanning rates: 100 mV s^{-1}.

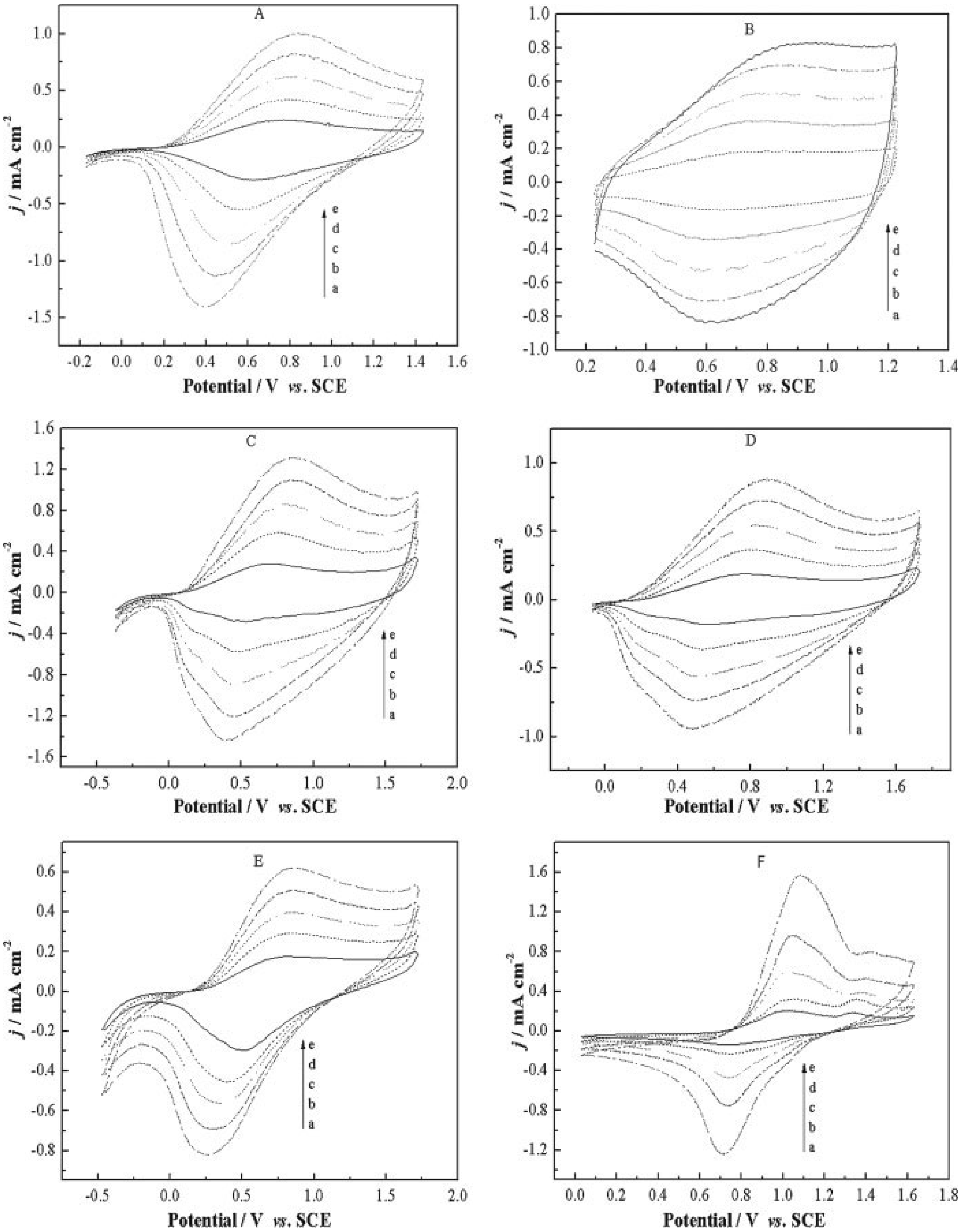


Figure 3 CVs of PTh films (A), poly(Th-*co*-DOF = 1 : 1) films (B), poly(Th-*co*-DOF = 2 : 1) films (C), poly(Th-*co*-DOF = 3 : 1) films (D), poly(Th-*co*-DOF = 5 : 1 films (E), PDOF films, and (F) recorded in BFEE at potential scan rates of 250 (a), 200 (b), 150 (c), 100 (d), and 50 (e) mV s^{-1}.

these two monomers implied that the copolymerization of DOF and Th may be feasible. To identify proper stoichiometries for copolymer formation, various feed ratios of Th and DOF were tested. When the feed ratio of Th/DOF was 5 : 1, the initial oxidation potential onset of the copolymer was at 1.35 V [Fig. 1(b)]. When the feed ratios of Th/DOF was 3 : 1, 2 : 1, and 1 : 1, the oxidation onsets of the copolymer were at 1.36, 1.39, and 1.40 V, respectively [Fig. 1(c–e)]. With the increase of thiophene concentration, the oxidation potential onsets of the copolymer shifted negatively. The oxidation potential onsets of the monomer mixtures between that of the two monomers suggested that the two monomers

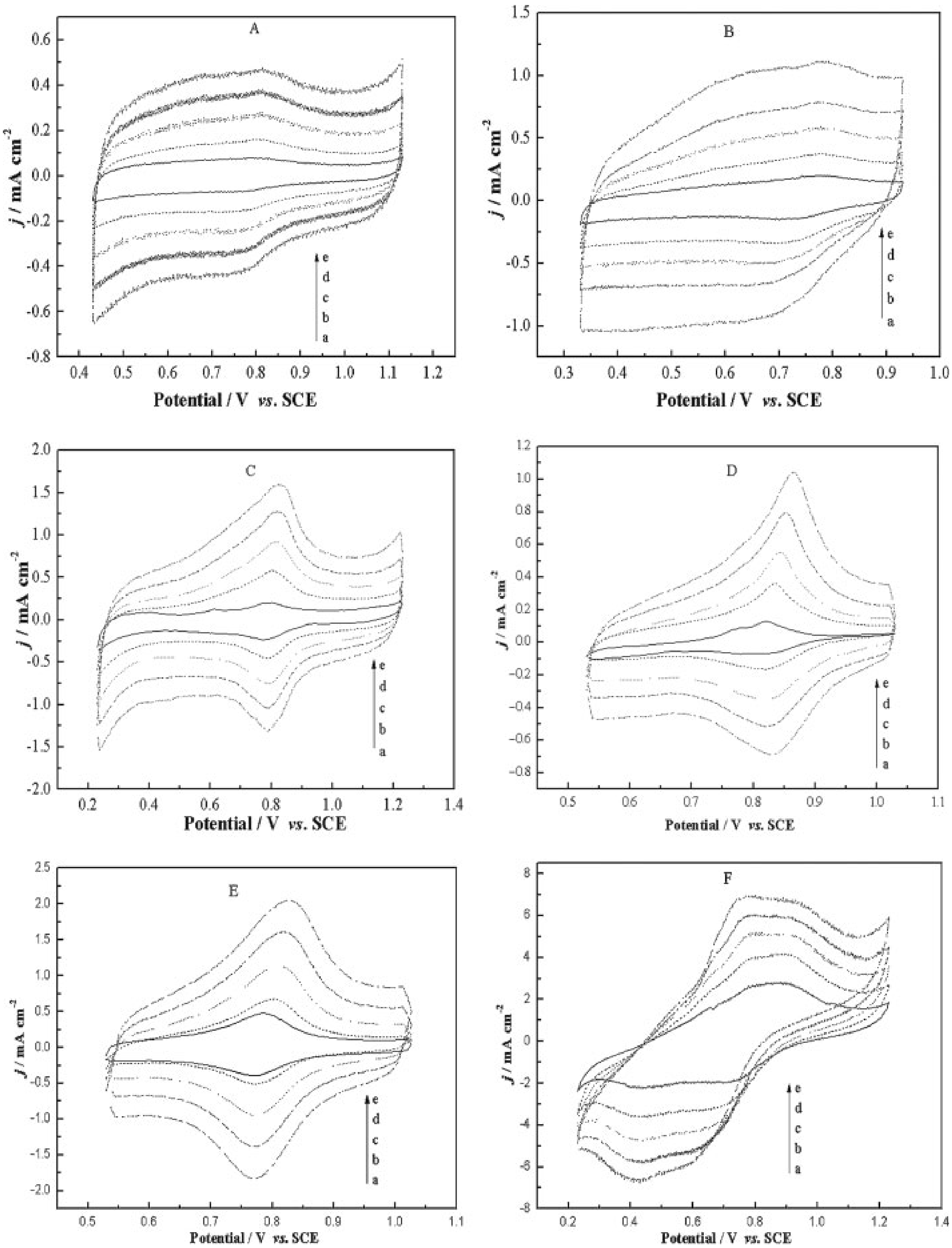


Figure 4 CVs of PTh films (A), poly(Th-*co*-DOF = 1 : 1) films (B), poly(Th-*co*-DOF = 2 : 1) films (C), poly(Th-*co*-DOF = 3 : 1) films (D), poly(Th-*co*-DOF = 5 : 1 films (E), PDOF films (F) recorded in 98% concentrated H_2SO_4 at potential scan rates of 250 (a), 200 (b), 150 (c), 100 (d), and 50 (e) mV s^{-1}.

were oxidized together and the copolymer chains may be composed of both DOF and Th units.

The successive cyclic voltammograms (CVs) of DOF, Th, and the mixture of the two monomers with various feed ratios in 80% BFEE + 20% EE solutions at a potential scanning rate of 100 mV s^{-1} were illustrated in Figure 2. As the CVs scan continues, CP films were also formed on the working electrode surface. The increase in the redox wave currents implied that the amount of the polymer on

TABLE I
The Redox Peak Potentials of PDOF, Poly(Th-*co*-DOF = 1 : 1), Poly(Th-*co*-DOF = 2 : 1), Poly(Th-*co*-DOF = 3 : 1), Poly(Th-*co*-DOF = 5 : 1), and PTh Measured in Pure BFEE and Concentrated Sulfuric Acid

	Pure BFEE		Concentrated sulfuric acid	
	E_{pa} (V)	E_{pc} (V)	E_{pa} (V)	E_{pc} (V)
PTh	0.83	0.39	0.82	0.76
Poly(Th-*co*-DOF = 1 : 1)	0.85	0.64	0.78	0.70
Poly(Th-*co*-DOF = 2 : 1)	0.84	0.41	0.83	0.80
Poly(Th-*co*-DOF = 3 : 1)	0.86	0.48	0.86	0.83
Poly(Th-*co*-DOF = 5 : 1)	0.82	0.26	0.83	0.77
PDOF	1.08	0.71	0.76	0.43

the electrode was increasing. The potential shift of the wave current maximum provides the information about the augmentation of the electrical resistance in polymer film and the overpotential required to overcome the resistance.[57] PTh can be reduced and oxidized between 0.23 V and 1.05 V [Fig. 2(a)]. The CVs of PDOF showed relatively narrow redox waves with the reduction and oxidation peaks at 0.95 V and 1.16 V [Fig. 2(f)]. In sharp contrast to PDOF, the oxidation and reduction potentials of the mixture both shift negatively. The CVs of mixtures with various feed ratios were similar to PTh [Fig. 2(b–e)]. This also indicates that Th is more favorable for polymerization. When taking the working electrode out of the electrolyte, polymers films were also found on the electrode surface.

Electrochemistry of copolymer films

In order to further prove the occurrence of copolymerization, further studies were carried out for PTh, PDOF, and the copolymer films prepared with various feed ratios at the constant applied potential of 1.55 V. The electrochemical properties of these polymer films were characterized by CVs in monomer-free BFEE solution (Fig. 3), 98% concentrated H_2SO_4 (Fig. 4), respectively.

In BFEE, PTh can be oxidized and reduced from 0.80 V to 0.39 V [Fig. 3(a)], PDOF can be oxidized or reduced from 1.05 V to 0.62 V [Fig. 3(f)]. With the increases of potential scanning rates, the redox potential of the polymers shifted significantly. The CVs of copolymers films prepared from feed ratios of Th/DOF were 1 : 1, 2 : 1, 3 : 1, 5 : 1 and showed redox potentials between those of PTh and PDOF, as shown in Table I. The value of oxidation peaks and reduction peaks were very close to each other, as shown in Figure 3(b–e). The results indicated that the copolymers films deposited on Pt wire had good redox reversibility and good redox activity. Similar results can also be observed in 98% concentrated H_2SO_4 (Fig. 4). All polymer films can be cycled repeatedly between the conducting and insulating state with no significant decomposition, indicating high structural stability of as-formed polymers and copolymers. A detailed summary of the oxidization and reduction potentials of these polymers in different electrolytes was listed in Table I. All these results indicated the good redox activity of the copolymer films in BFEE or concentrated sulfuric acid, confirming the occurrence of copolymerization.

Structural characterizations

During the potentiostatic process, the color of solution around the electrode darkened gradually. With the polymerizing propagation, part of the soluble oligomers became insoluble and deposited on the working electrode, with the elongation of the polymer main chain. However, some oligomers still diffused from the electrode into the bulk solution, making the solution color-darkened. PDOF film changed its color from dark brownish red in the doped state to brown in the dedoped state, and it can partly dissolve in organic solvents such as DMSO and THF. PTh film changed its color from black in doped state to dark brownish red in dedoped state and never dissolved in organic solvents. For the copolymers, their colors changed from dark black in doped state to gray in the dedoped state, and were almost insoluble in all organic solvents.

The UV–visible spectra of the dedoped PTh, PDOF, and copolymer films deposited on ITO electrode were shown in Figure 5. The spectra of PTh films showed characteristic absorptions of 465 and 785 nm [Fig. 5(a)]. The band at 785 nm was the characteristic of conductive species, such as the existence of po-

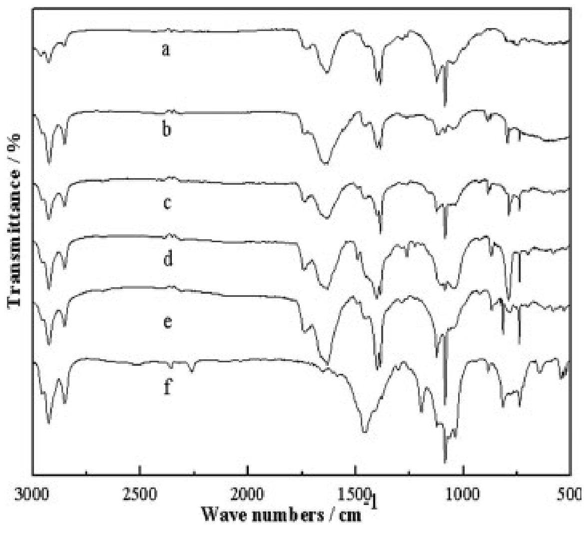


Figure 5 UV–visible spectra of PTh (a), poly(Th-*co*-DOF = 1 : 1) (b), poly(Th-*co*-DOF = 2 : 1) (c), poly(Th-*co*-DOF = 3 : 1) (d), poly(Th-*co*-DOF = 5 : 1 (e), and PDOF (f) films coated on an ITO in the doped states.

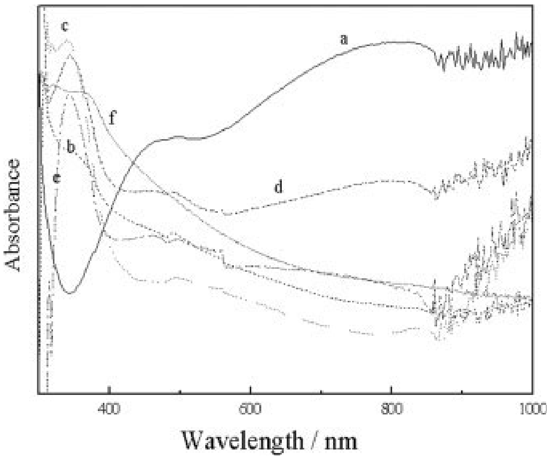


Figure 6 Infrared spectra of PTh (a), poly(Th-*co*-DOF = 1 : 1) (b), poly(Th-*co*-DOF = 2 : 1) (c), poly(Th-*co*-DOF = 3 : 1) (d), poly(Th-*co*-DOF = 5 : 1) (e), and PDOF (f) films in dedoped state films.

laron or bipolaron. The spectra of PDOF films show a broad absorption from 305 to 378 nm [Fig. 5(f)]. The absorption was derived from a valence band-conductive band (π-π*) transition. On the other hand, the spectra of the copolymers films showed both the characteristic absorptions of PDOF and PTh, located at 341 and 490 nm, respectively [Fig. 5(b–e)], further confirming the occurrence of the copolymerization.

FT-IR spectrum can provide structural information about the neutral CPs, especially for those that are insoluble and infusible. The comparison on the evolution of the vibrational modes appearing in CPs usually facilitates the interpretation of the polymerization process. PTh, PDOF, and copolymers prepared from BFEE containing 20% EE solution were also analyzed by FT-IR spectroscopy (Fig. 6). According to the spectrum of PTh [Fig. 6(a)], the Th ring stretching modes were observed at 1742 and 1634 cm^{-1}. According to the spectrum of PDOF [Fig. 6(f)], the bands at 885, 816, and 738 cm^{-1} indicated the existence of a 1,2,4-trisubstituted benzene ring in PDOF.[58] According to the spectra of copolymers, the band at 1742, 1634, 885, 816, 738 cm^{-1} coexisted, further confirming the successful copolymerization of Th and DOF.

Fluorescence properties

Literature reported that PTh and its derivatives were good green–red light emitter.[1–5] Dedoped PTh in our experiment shows no emission in the whole range. The main reason for this phenomenon of freestanding PTh film electrodeposited from BFEE solution may be the tailer of PTh main backbone, which quenches the photoluminescence properties of PThs.[59]

On the other hand, PDOF films have two main peaks at 400 and 417 nm, implying a good blue-light-emitting material in well accordance with previous reports on the fluorescence properties of polyfluorenes.[2,4,6–8,46] Doped copolymers films exhibited four main peaks at about 392, 435, 467, and 494 nm when excited by 330 nm (Fig. 7, Table II). In comparison with the emission peaks of PDOF, the emission spectra of the copolymer prepared by monomer ratio of thiophene and DOF of 1 : 1 [Fig. 7(c)] showed emission peaks at 435 nm. This indicated that the incorporation of thiophene unit in the PDOF main backbone made the emission peaks of doped copolymer redshifted about 35 nm. Increasing the thiophene ratios during the electrocopolymerization from 1 : 1 to 2 : 1, 3 : 1, 5 : 1, the emission peaks of the copolymers showed further redshift, gradually to the emission peaks at about 435 and 467 nm, as can be seen clearly in Figure 7. This is mainly because the narrow band-gap thiophene was incorporated into the copolymer backbone. In addition, these results implied that by the incorporation thiophene structural unit in the doped copolymer main back-

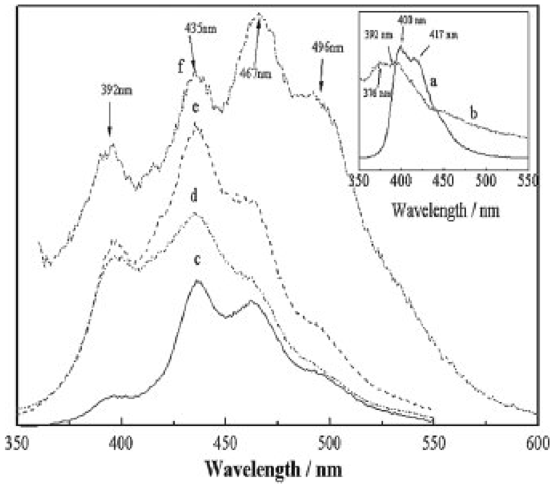


Figure 7 Fluorescence spectra of doped polymer films of PDOF (a), PTh (b), poly(Th-*co*-DOF = 1 : 1) (c), poly(Th-*co*-DOF = 2 : 1) (d), poly(Th-*co*-DOF = 3 : 1) (e), and poly (Th-*co*-DOF = 5 : 1 (f) films coated on an ITO in solid state.

TABLE II
The Fluorescence Properties of PDOF, Poly(Th-*co*-DOF = 1 : 1), Poly(Th-*co*-DOF = 2 : 1), Poly(Th-*co*-DOF = 3 : 1), Poly(Th-*co*-DOF = 5 : 1), and PTh

	Fluorescence	
	In doped sates (nm)	In dedoped sates (nm)
PTh		376, 392
Poly(Th-*co*-DOF = 1 : 1)	392, 432, 462, 494	378, 395
Poly(Th-*co*-DOF = 2 : 1)	392, 433, 463, 495	375, 395
Poly(Th-*co*-DOF = 3 : 1)	392, 434, 465, 495	376, 395
Poly(Th-*co*-DOF = 5 : 1)	392, 435, 467, 496	377, 394
PDOF		400, 417

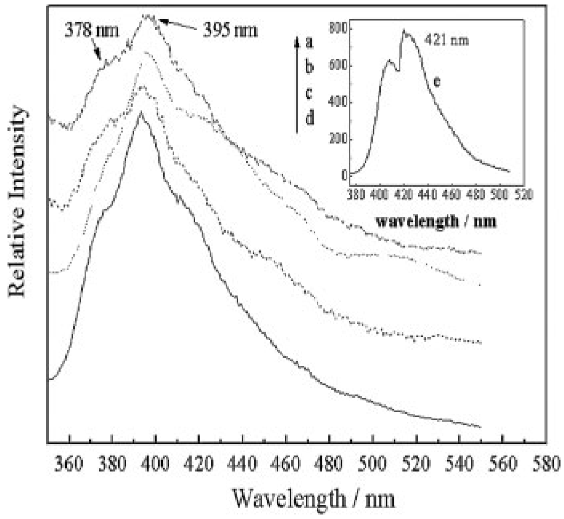


Figure 8 Fluorescence spectra of dedoped polymer films of poly(Th-*co*-DOF = 1 : 1) (a), poly(Th-*co*-DOF = 2 : 1) (b), poly(Th-*co*-DOF = 3 : 1) (c), poly(Th-*co*-DOF = 5 : 1) (d), and PDOF (e) in solid states.

bone, the goal of tuning fluorescence can be basically achieved.

The fluorescence spectra of dedoped copolymers films showed maximum emissions at about 378 and 394 nm when excited by 335 nm (Fig. 8, Table II). This can be assigned to the conjugated copolymer main chains. The valid conjugation chain length of the dedoped copolymer films produced in the same condition is similar to each other, or the tailer of the copolymers in dedoped state, which results in the similar fluorescence spectra of dedoped copolymer films. Therefore, the peak position in the fluorescence spectra is unanimous basically. Furthermore, PTh has the advantage of ease of electrodeposition of free-standing films with high conductivity. Combining these advantages together, the copolymer of DOF and thiophene may be good candidates for applications such as blue–green light-emitting materials.

Thermal analysis

The degradation behaviors of CPs are very important for their potential applications. In order to investigate the thermal stability of polymer films prepared in BFEE + 20% EE, thermal analysis of PTh and copolymers films were performed, as shown in Figure 9. The PTh and copolymers films used for thermal analysis the polymerization were carried out under potentiostatic conditions (E = 1.55 V). All thermal analysis was performed under a nitrogen stream in the temperature range of 300–1100 K, at a heating rate of 10 K min^{-1}. It can be seen from this figure that PTh film started to lose weight when the temperature reached 528 K. The decomposition was up to 45% when the temperature reached 650 K [Fig. 9(a)]. This weight loss was attributed to the degradation of the skeletal PTh backbone chain structure. The comparison of these data of PDOF and PTh indicated that free-standing PTh films had better thermal stability than that of PDOF films. The copolymer started to lose weight at about 532 K, very close to PTh. The decomposition of poly (Th-*co*-DOF =2 : 1) is the fastest, up to 7.5% between 678 and 755 K. This weight loss was attributed to the degradation of the skeletal poly (Th-*co*-DOF =2 : 1) backbone chain structure. Other small decomposition occurred between 800 and 1078 K, possibly because of the overflow of some oligomers that decomposed from the copolymer with temperature increases. Similar results can also be observed from other copolymers, indicating good thermal stability of copolymers.

Conductivity and solubility

The conductivities of PTh, PDOF, and the copolymers obtained potentiostatically in BFEE + 20% EE were measured (Table III). Freestanding PTh exhibited excellent conductivity, up to 48 S cm^{-1}.[32] On the contrary, the conductivity of PDOF was only about 1 × 10^{-2} S cm^{-1}.[46] With the increases of Th contents in the copolymer, the conductivities of the copolymer increased gradually, as shown in Table III. This indicated that more incorporation of Th units into PDOF chain was helpful for improving the conductivity of PF, which may be beneficial to extend the application of PDOF. PTh and all copolymers are not soluble in all solvents (DMSO, THF, $CHCl_3$, and hexane) used in this study. On the

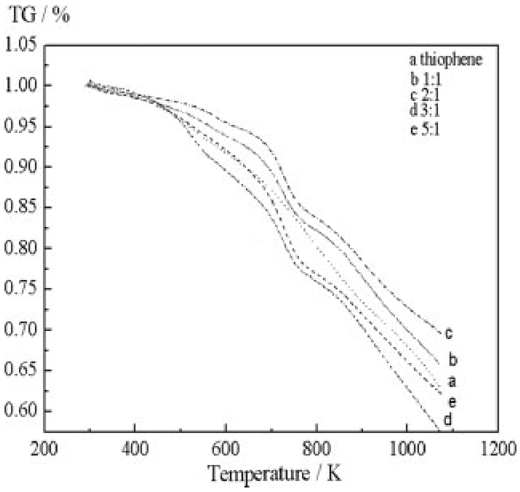


Figure 9 TG curves of PTh film (a), poly(Th-*co*-DOF = 1 : 1) film (b), poly(Th-*co*-DOF = 2 : 1) film (c), poly(Th-*co*-DOF = 3 : 1) film (d), poly(Th-*co*-DOF = 5 : 1) film (e), and PDOF films (f), respectively.

TABLE III
The Electrical Conductivities of PDOF, PTh, and Copolymers Films Prepared in 80% BFEE + 20% EE at the Constant Applied Potentials of 1.55 V

	Conductivity (S cm^{-1})
Polythiophene	48.7[29]
Poly(Th-*co*-DOF = 1 : 1)	1.02
Poly(Th-*co*-DOF = 2 : 1)	3.31
Poly(Th-*co*-DOF = 3 : 1)	5.22
Poly(Th-*co*-DOF = 5 : 1)	8.32
PDOF	0.01

contrary, PDOF is soluble in all aforementioned solvents.

The quality of PTh films was quite good, and it can be peeled off the electrode in free-standing state. It can be easily cut into various shapes by a knife.[29,32] The quality of PDOF film was not quite good enough.[46] The copolymerization of DOF and Th has greatly improved the quality of copolymer film (typical as Fig. 10), as free-standing films can be peeled off the electrode. The high quality and free-standing copolymer poly(DOF-*co*-Th) together good fluorescence properties may be greatly helpful for application in PLEDs as blue–green light-emitting materials.

CONCLUSIONS

In this article, electrochemical copolymerization of Th and DOF was successfully realized in BFEE + 20% EE solution by the direct anodic oxidation of the monomer mixtures. The properties of as-formed high quality poly(DOF-*co*-Th) films depended on the feed ratio of monomer mixtures. Freestanding PThs and poly(Th-*co*-DOF) films can be easily produced. Incorporation of Th into PDOF chain allowed overcoming the low conductivity deriving from the poor quality of PDOF film. Copolymer films showed both the good properties of PDOF and PTh, such as good redox activity, electrical conductivity, thermal stability, and good film quality. Fluorescence studies revealed that the dedoped copolymer were good blue-light emitters, with a maximum emission at 395 nm and a shoulder at 378 nm in solid state, while doped copolymers were good blue–green light emitters.

Figure 10 Photograph of free-standing poly(Th-*co*-DOF = 1 : 1) films electrodeposited on the electrode surface from 80% BFEE containing 20% EE solution at a constant applied potential of 1.55 V vs. SCE.

References

1. Scherf, U.; List, E. J. W. Adv Mater 2002, 14, 477.
2. Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. Adv Mater 2000, 12, 1737.
3. Mishima, K.; Yamashita, K. J Phys Chem A 2001, 105, 2867.
4. Zeng, G.; Yu, W. L.; Chua, S. J.; Huang, W. Macromolecules 2002, 35, 6907.
5. Kulkarni, A. P.; Zhu, Y.; Jenekhe, S. A. Macromolecules 2005, 38, 1553.
6. Li, B.; Li, J.; Fu, Y. Q.; Bo, Z. S. J Am Chem Soc 2004, 126, 3430.
7. Chen, X. W.; Liao, J. L.; Liang, Y. M.; Ahmed, M. O.; Tseng, H. E.; Chen, S. A. J Am Chem Soc 2003, 125, 636.
8. Prieto, I.; Teetsov, J.; Fox, M. A.; Vanden Bout, D. A.; Bard, A. J. J Phys Chem A 2001, 105, 520.
9. Teetsov, J.; Vanden Bout, D. A. J Phys Chem B 2000, 104, 9378.
10. Schuta, P.; Caruso, F. Langmuir 2001, 17, 7670.
11. Tak, Y. H.; Bassler, H.; Leuninger, J.; Mullen, K. J Phys Chem B 1998, 102, 4887.
12. Cao, Y.; Parker, I. D.; Yu, G.; Zhang, C.; Heeger, A. J. Nature (London) 1999, 397, 414.
13. Kim, Y. C.; Lee, T. W.; Park, O. O.; Kim, C. Y.; Chao, H. N. Adv Mater 2001, 13, 646.
14. Lee, Y. Z.; Chen, X.; Chen, S. A.; Wei, P. K.; Fann, W. S. J Am Chem Soc 2001, 123, 2296.
15. Ahn, T.; Song, S. Y.; Shim, H. K. Macromolecules 2000, 33, 6764.
16. Liu, B.; Niu, Y. H.; Yu, W. L.; Cao, Y.; Huang, W. Synth Met 2002, 129, 129.
17. Boogaard, M.; Bonnet, G.; Hof, A.; Wang, Y.; Brochon, C.; Hutten, P.; Lapp, A.; Hadziioannou, G. Chem Mater 2004, 16, 4383.
18. Cao, D. R.; Liu, Q. L.; Zeng, W. J.; Han, S. H.; Peng, J. B.; Liu, S. P. Polym Sci Part A: Polym Chem 2006, 44, 2395.
19. Roncali, J. Chem Rev 1992, 92, 711.
20. Groenendaal, L. G.; Jonas, F.; Pielartzik, H.; Reynolds, J. R. Adv Mater 2000, 12, 481.
21. Mccullogh, R. D. Adv Mater 1998, 10, 93.
22. Groenendaal, L. G.; Zotti, P. H.; Aubert, S. M. Waybright, J. R. R. Adv Mater 2003, 15, 855.
23. Jin, S.; Xue, G. Macromolecules 1997, 30, 5753.
24. Chen, W.; Xue, G. Prog Polym Sci 2005, 30, 783.
25. Xu, J. K.; Shi, G. Q.; Qu, L. T.; Zhang, J. X. Synth Met 2003, 136, 221.
26. Wan, X. B.; Liu, X.; Xue, G.; Jiang, L. X.; Hao, J. J. Polymer 1999, 40, 4907.
27. Liu, C.; Zhang, J. X.; Shi, G. Q.; Zhao, Y. F. J Phys Chem B 2004, 108, 2195.
28. Wan, X. B.; Yan, F.; Jin, S.; Liu, X. R.; Xue, G. Chem Mater 1999, 11, 2400.
29. Shi, G. Q.; Jin, S.; Xue, G.; Li, C. Science 1995, 267, 994.
30. Li, C.; Shi, G. Q.; Liang, Y. Q.; Ye, W.; Sha, Z. L. Polymer 1997, 38, 5023.

31. Wang, X. F.; Shi, G. Q.; Liang, Y. Q. Electrochem Comm 1999, 1, 536.
32. Shi, G. Q.; Li, C.; Liang, Y. Q. Adv Mater 1999, 11, 1145.
33. Li, C.; Shi, G. Q.; Liang, Y. Q. J Electroanal Chem 1998, 455, 1.
34. Shi, G. Q.; Xue, G.; Li, C.; Jin, S. Polym Bull 1994, 33, 325.
35. Huang, Z. M.; Qu, L. T.; Shi, G. Q.; Chen, F. E.; Hong, X. Y. J Electroanal Chem 2003, 556, 159.
36. Fan, B.; Qu, L. T.; Shi, G. Q. J Electroanal Chem 2005, 575, 287.
37. Xu, J. K.; Nie, G. M.; Zhang, S. S.; Han, X. J.; Hou, J.; Pu, S. Z. J Polym Sci A: Polym Chem 2005, 43, 1444
38. Xu, J. K.; Zhou, W. Q.; Hou, J.; Pu, S. Z.; Yan, L. S.; Wang, J. W. J Polym Sci A: Polym Chem 2005, 43, 3986.
39. Xu, J. K.; Zhou, W. Q.; Hou, J.; Pu, S. Z.; Yan, L. S.; Wang, J. W. Mater Lett 2005, 59, 2412.
40. Xu, J. K.; Zhou, W. Q.; Hou, J.; Pu, S. Z.; Yan, L. S.; Wang, J. W. Chin J Polym Sci 2006, 24, 53.
41. Xu, J. K.; Wei, Z. H.; Hou, J.; Pu, S. Z. Acta Polym Sinica 2006, 3, 474.
42. Pu, S. Z.; Hou, J.; Xu, J. K.; Nie, G. M.; Zhang, S. S.; Shen, L.; Xiao, Q. Mater Lett 2005, 59, 1061.
43. Xu, J. K.; Hou, J.; Zhang, S. S.; Nie, G. M.; Pu, S. Z.; Shen, L.; Xiao, Q. J Electroanal Chem 2005, 578, 345.
44. Shen, L.; Xu, J. K.; Wei, Z. H.; Xiao, Q.; Pu, S. Z. Eur Polym J 2005, 41, 1738.
45. Xu, J. K.; Zhang, Y. J.; Hou, J.; Wei, Z. H.; Pu, S. Z.; Zhao, F.; Du, Y. K. Eur Polym J 2006, 42, 1154.
46. Xu, J. K.; Zhang, Y. J.; Wei, Z. H.; Zhou, W. Q.; Zhao, J. Q. Acta Chim Sinica 2006, 64, 911.
47. Wan, X. B.; Zhang, W.; Jin, S.; Xue, G.; You, Q. D.; Chen, B. J Electroanal Chem 1999, 470, 23.
48. Wan, F.; Li, L.; Wan, X. B.; Xue, G. J Appl Polym Sci 2002, 85, 814.
49. Shi, G. Q.; Zhang, J. X.; Chen, F. E.; Xu, J. K.; Hong, X. Y. Acta Chim Sinica 2001, 59, 1818.
50. Li, L.; Chen, W.; Xu, N.; Xiao, Z. G.; Xue, G. J Mater Sci 2004, 39, 2395.
51. Xu, J. K.; Wei, Z. H.; Xiao, Q.; Pu, S. Z. Chin J Polym Sci 2006, 3, 253.
52. Zhou, L.; Li, Y. Q.; Xue, G. Thin Solid Films 1998, 335, 112.
53. Nie, G. M.; Xu, J. K.; Zhang, S. S.; Cai, T.; Han, X. J. J Appl Polym Sci 2006, 102, 1877.
54. Xu, J. K.; Nie, G. M.; Zhang, S. S.; Han, X. J.; Hou, J.; Pu, S. Z. J Mater Sci 2005, 40, 2867.
55. Wei, Z. H.; Xu, J. K.; Pu, S. Z.; Du, Y. K. J Polym Sci A: Polym Chem 2005, 44, 4904.
56. Assaka, A.; Rodrigues, P.; Oliverira, A.; Ding, L.; Hu, B.; Akcelrud, L. Polymer 2004, 45, 7071.
57. Otero, T. F.; Larreta, E. D. Polymer 1988, 29, 1522.
58. Rong, G. B.; Zhu, S. Z. Structure Determination of Organic Compounds Tables of Spectral Data; Eastchina University of Science and Technology: Shanghai, 2002; pp 255–265 (in Chinese).
59. Perpichka, I. F.; Perpichka, D. F.; Meng, H.; Wudl, F. Adv Mater 2005, 17, 2281.