

# Low Potential Electrodeposition of High-Quality and Freestanding Poly(3-(6-Bromohexyl)Thiophene) Films

Jingkun Xu,<sup>1</sup> Zhenhong Wei,<sup>1</sup> Yukou Du,<sup>2</sup> Shouzhi Pu,<sup>1</sup> Jian Hou,<sup>1</sup> Weiqiang Zhou<sup>1</sup>

<sup>1</sup>Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, Jiangxi Province, People's Republic of China

<sup>2</sup>Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006 Jiangsu Province, People's Republic of China

Received 28 October 2005; accepted 19 March 2006

DOI 10.1002/app.24576

Published online 23 April 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** High-quality freestanding and conducting poly[3-(6-bromohexyl)thiophene] (PBHT) films with electrical conductivity of 20 S/cm were synthesized electrochemically by direct anodic oxidation of 3-(6-bromohexyl)thiophene (BHT) in boron trifluoride diethyl etherate (BFEE). The oxidation potential of BHT in pure BFEE was measured to be only 1.2 V versus saturated calomel electrode, SCE much lower than that determined in acetonitrile (ACN) (1.8 V vs SCE). The polymer films obtained from this media were very shiny and flexible and can be easily cut into various shapes. The structure and morphol-

ogy of the polymer films were investigated by UV-vis, infrared, <sup>1</sup>H-NMR spectroscopy, thermal analysis, and scanning electron microscopy (SEM). All these results indicated that the terminal bromide did not have negative effect on the electrochemical polymerization of BHT. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1570–1576, 2008

**Key words:** inherently conducting polymers; polythiophenes; 3-(6-bromohexyl)thiophene; boron fluoride diethyl etherate; electrochemical polymerization

## INTRODUCTION

During the past 25 years, inherently conducting polymers, such as poly(*para*-phenylene),<sup>1,2</sup> polyaniline,<sup>3</sup> and polypyrrole,<sup>4–6</sup> have attracted great attention due to their wide fundamental interest and potential application in electronics, electrocatalysis, and pharmacology. Among them, polythiophene and its derivatives exhibited favorable electrochromic properties and were currently the focus of large portion of research in this field and a significant much of polymers have already been obtained.<sup>7–16</sup> However, the oxidation potentials of thiophene in common electrochemical solvents such as acetonitrile and CH<sub>2</sub>Cl<sub>2</sub>, are usually very high. The qualities of films obtained from common media were very poor. To overcome this so-called “polythiophene paradox,” boron trifluoride diethyl etherate (BFEE) had been used for the electrochemical polymerization of thiophenes. The interaction between BFEE and the aromatic monomers can lower the monomer oxidation potentials. Moreover, the catalytic effect of BFEE facilitates the formation of high-quality freestanding polythiophene films. A set of freestanding films of polythiophene and its

derivatives with good mechanical, electrical and thermal properties have been electrodeposited.<sup>17–25</sup> Under these circumstances, BFEE serves not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte was needed (ionic conductivity of freshly distilled BFEE was ~400 μS/cm). Moreover, the substitution of thiophene on the 3-position with electron-donating substituents can further decrease the monomer oxidation potentials.<sup>26–35</sup> The electron-donating ability of the substituents greatly affects the oxidation of the monomer. According to the literature,<sup>24</sup> there is a linear relationship between the Hammett constant of the substituent and the oxidation potentials of the monomer. For example, the oxidation potential of thiophene in BFEE was 1.37 V vs saturated calomel electrode (SCE),<sup>17</sup> which was lower than that of 3-bromothiophene (1.56 V vs SCE),<sup>27</sup> monomer substituted with electron withdrawing group. The substitution by electron-donating groups also led to the decreases of the monomer oxidation potentials, such as 3-methylthiophene (1.30 V vs SCE)<sup>28</sup> and 3-octylthiophene (1.17 V vs SCE).<sup>30</sup>

To obtain more β-substituted monomers, 3-bromohexylthiophene (BHT) may be a very interesting and useful starting material. The terminal bromide atom at the end of alkyl chain is a very active group and can react with other functional groups. For example, it can use the bridge bromide to connect with other

Correspondence to: J. Xu (xujingkun@tsinghua.org.cn).

monomers, such as fluorene<sup>36</sup> and 3,4-ethylenedioxythiophene methanol.<sup>37</sup> So many new copolymers with properties intermediate between the individual polymers can be obtained. Furthermore, the long alkyl chain can increase the solubility of polymer in organic solvents. However, the electrochemical polymerization of BHT has not been reported yet. In the present work, BHT was electrochemically polymerized in BFEE and high-quality freestanding PBHT can be obtained with conductivity of 20 S/cm. The thermal stability and spectroscopic properties of the polymer were also investigated in detail.

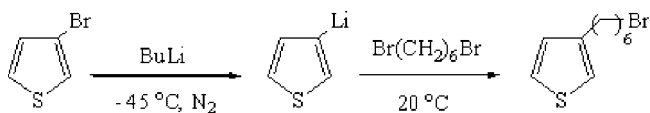
## EXPERIMENTAL

### Materials

3-(6-Bromohexyl)thiophene (BHT) was synthesized by reaction of 3-bromothiophene with 1,6-dibromohexane in hexane solution using BuLi as reducing agent under the atmosphere of N<sub>2</sub> as illustrated in Scheme 1.<sup>38</sup> Tetrabutylammonium tetrafluoroborate (TBATFB, Acros Organics (Fair Lawn, NJ, USA) 95%) was dried in vacuum at 60°C for 24 h. Boron trifluoride diethyl etherate (BFEE, Beijing Changyang Chemical Plant, Beijing, People's Republic of China) was distilled and stored at -20°C before use. Commercial HPLC-grade acetonitrile (ACN) was made by Tianjin Guangfu Fine Chemical Institute (Tianjin, People's Republic of China) and was used directly without further purification.

### Electrochemical experiments

Electrochemical synthesis and examination 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 wires and stainless steel wires with a diameter of 0.5 mm and 1 mm, placed 0.5 cm apart, respectively. For large-scale polymer film production, stainless steel sheets with a surface area of 4 cm<sup>2</sup> was employed as working electrode and counter electrodes, which were carefully polished with abrasive paper (1500 mesh) and subsequently cleaned by water and acetone successively before each examination. The polymers were deposited on an indium-tin-oxide (ITO)-coated glass for UV-visible spectra measurements. All potentials were referred to an SCE.



**Scheme 1** Synthesis route of BHT monomer.

The typical solution was BFEE containing 0.05 mol L<sup>-1</sup> BHT. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during experiments. The amount of polymer deposited on the electrode was controlled by the integrated charge passed through the cell. To remove the electrolyte and oligomers/monomer, the polymer films were rinsed with ammonia and acetone. For spectral analysis, the polymer was dried under vacuum at 60°C for 2 days.

### Characterizations

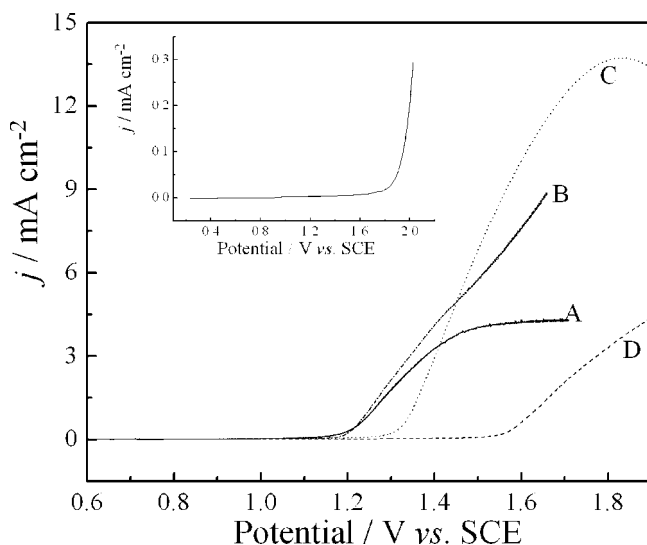
The electrical conductivity of PBHT films was measured by conventional four-probe technique. UV-visible spectra were taken by using Perkin-Elmer Lambda 900 UV-vis-NIR spectrophotometer. Infrared spectra were recorded using Bruker Vertex 70 FT-IR spectrometer with KBr pellets. The <sup>1</sup>H-NMR spectra were recorded on a Bruker AV 400 NMR spectrometer and CDCl<sub>3</sub> was used as the solvent. The thermogravimetric (TG) analysis was performed with a thermal analyzer of Netzsch TG 209. Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6700F scanning electron microscopy.

## RESULTS AND DISCUSSION

### Electrochemical polymerization

Figure 1 shows the anodic polarization curves of thiophene derivatives in pure BFEE and that of BHT in ACN + 0.1 M TBATFB. The oxidation onset of BHT was initiated at 1.2 V [Fig. 1(A)], which was much lower than that of BHT in ACN + 0.1 M TBATFB at 1.8 V (Fig. 1, insert). This implied that the oxidation of BHT in BFEE was much easier than that in ACN/TBATFB. According to the Figure 1, the oxidation onset of BHT was nearly equal to those of 3-octylthiophene at 1.17 V [Fig. 1(B)] and 3-methylthiophene at 1.30 V [Fig. 1(C)] but obviously lower than that of 3-bromothiophene at 1.56 V [Fig. 1(D)]. The similarity of the oxidation potentials of 3-octylthiophene and BHT implies that the terminal bromide did not affect the anodic oxidation of BHT, especially in comparison with 3-bromothiophene.

The successive cyclic voltammograms (CVs) of 0.05 mol L<sup>-1</sup> BHT on a Pt electrode in BFEE were shown in Figure 2. It is clearly shown in Figure 2 that on the first CV cycle, the current on the reverse scan was higher than that on the forward scan. The formation of this loop was characteristic of nucleation processes and only appeared on the first CV cycle.<sup>39</sup> At the same time, with the potential scans continues, a polymer film was formed on the electrode surface. In BFEE, PBHT can be reduced and oxidized between 0.35 and 0.9 V. The increases of



**Figure 1** Anodic polarization curves of BHT (A), 3-octylthiophene (B), 3-methylthiophene (C), 3-bromothiophene (D) in BFEE solution and BHT in ACN + 0.1 M TBATFB (insert) containing 0.05 M monomers. Potential scan rate:  $20 \text{ mV s}^{-1}$ .

the redox wave currents implied that the amount of the polymer on the electrode surface has increasing. The potential shift of this maximum provided information about the increase of the electrical resistance in the polymer film and the over-potential was needed to overcome the resistance. All these phenomena indicated that high-quality PBHT films were formed on the anode surface. On the contrary, the successive CVs of BHT in ACN containing 0.1 M TBATFB were not very successful. No apparent redox waves were found, indicated only a trace amount of polymer was formed. This can be mainly ascribed to its high anodic oxidation potential together with the poor quality of as-formed polymer films.

### Electrochemistry of PBHT films

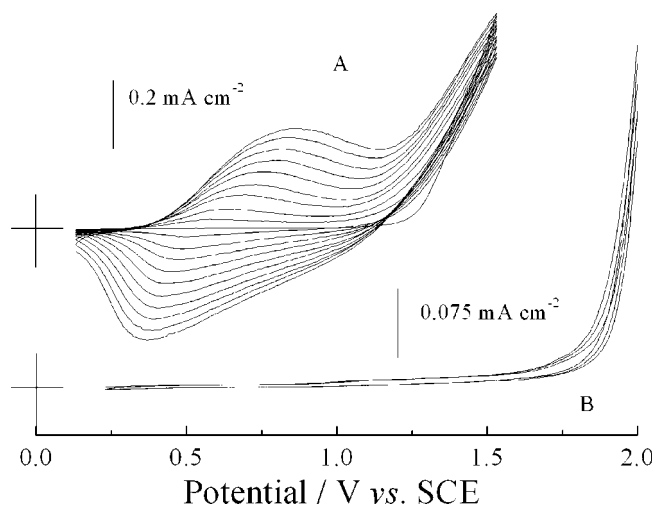
The electrochemical behavior of PBHT films deposited electrochemically from pure BFEE were studied in BFEE [Fig. 3(A)], ACN + 0.1 M TBATFB [Fig. 3(B)] and concentrated sulfuric acid [Fig. 3(C)], respectively. Similar to the results in the literature, the CVs represented broad anodic and cathodic peaks [Fig. 3(A)]. Peak current densities were both proportional to the scan rates (Fig. 3, insert), indicating the reversible redox behavior of the polymer. Furthermore, the anodic and cathodic peak potentials of the polymer films were independent on the scan rates, which suggested that the redox reactions were both reversible. These films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the material indicating the high stability of the

polymer. Similar results can be observed for the electrochemistry of PBHT in ACN [Fig. 3(B)] and concentrated sulfuric acid [Fig. 3(C)]. According to Figure 3A, the films obtained from pure BFEE can be oxidized and reduced from 1.0 to 0.35 V. However, much higher potentials (1.25–1.05 V) were needed to oxidize or reduce the films in ACN + 0.1 M TBATFB. In concentrated sulfuric acid, the anodic and cathodic peaks located at  $\sim 0.8$  and 0.32 V, respectively. All these results indicated the good stability of PBHT films in BFEE, ACN and even in concentrated sulfuric acid.

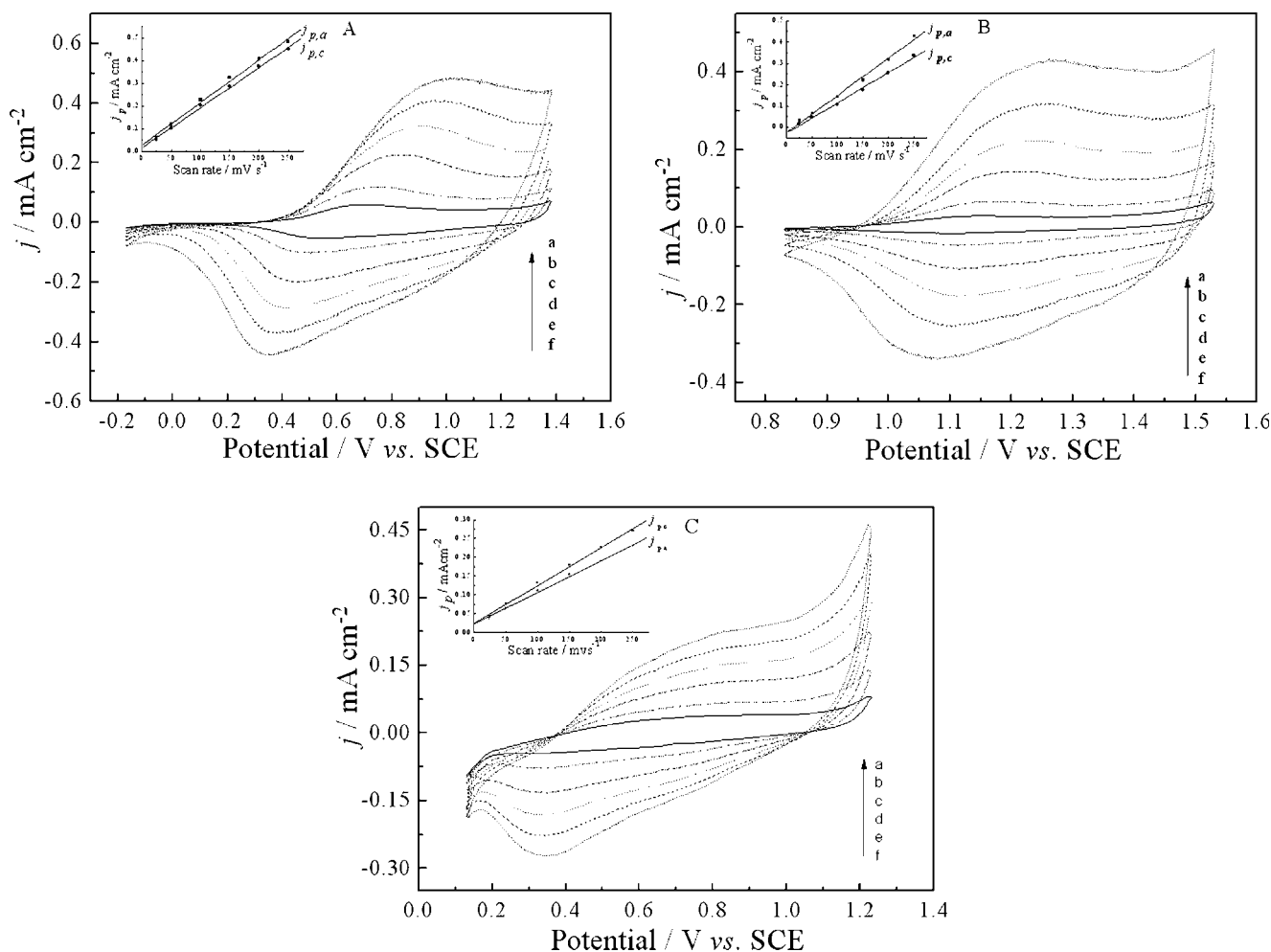
### Structural characterizations

As-formed PBHT films were very smooth, compact, black in the doped state and dark red in the dedoped state. The doped polymer film did not dissolve in common organic solvents, such as  $\text{CH}_2\text{Cl}_2$ , THF, DMSO. In contrast, the solubility of the dedoped film was also very little in these organic solvents as same as poly(3-octylthiophene). This is a great disadvantage of the application of PBHT because of its low solubility. However, this also implies the high quality of as-formed PBHT films prepared from BFEE solution.

The UV-visible spectra of BHT monomer (insert) recorded in  $\text{CH}_2\text{Cl}_2$  solution and PBHT films obtained on the ITO electrode were illustrated in Figure 4. The UV spectrum of the monomer showed a main peak at 235 nm. The spectrum of the polymer film has a much broad band with fine structure at 400 nm and 750 nm. The overall absorption tails off to about 780 nm. The longer wavelength indicated longer polymer sequences.<sup>40</sup> The band at 400 nm can be ascribed to the valence band-conduction band



**Figure 2** Cyclic voltammograms of 0.05 M BHT in pure BFEE (A) and in ACN + 0.1 M TBATFB (B). Potential scan rates:  $100 \text{ mV s}^{-1}$ .



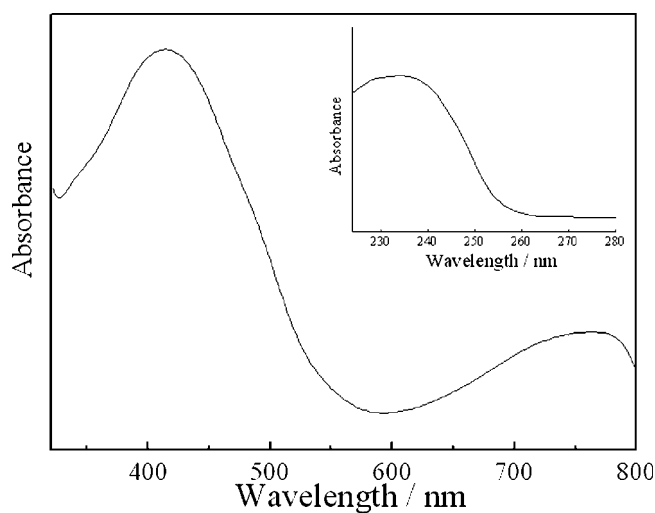
**Figure 3** Cyclic voltammograms of PBHT films in pure BFEE (A), ACN + 0.1 M TBATFB (B) and concentrated sulfuric acid (C), respectively. Potential scan rates: 25  $\text{mV s}^{-1}$  (a), 50  $\text{mV s}^{-1}$  (b), 100  $\text{mV s}^{-1}$  (c), 150  $\text{mV s}^{-1}$  (d), 200  $\text{mV s}^{-1}$  (e), 250  $\text{mV s}^{-1}$  (f). The polymer films were synthesized electrochemically in BFEE at a constant applied potential of 1.43 V.

( $\pi$ - $\pi^*$ ) transition. In contrast, the broad band from 580 to 782 nm is the characteristic of conductive species such as the existence of polaron or bipolaron. During the doping process, the originally filled valence band of PBHT becomes partially empty. The Fermi level lowers the valence band, which ensures a metallic behavior to the PBHT.<sup>41,42</sup> In this circumstance, it could be expected that at higher doping level, more empty the valence band would become of PBHT film. As a consequence, the polaron (or bipolaron) concentration will increased together with the conductivity increases.

Vibrational spectra can provide structural information on neutral and doped conducting polymers, especially for those insoluble and infusible. BHT monomer and PBHT films prepared potentiostatically from pure BFEE solution containing 0.05 mol  $\text{L}^{-1}$  BHT were analyzed by Fourier transform infrared (FT-IR) spectroscopy. According to the spectrum of the monomer [Fig. 5(A)], the bands at 2925 and 2855  $\text{cm}^{-1}$  can be ascribed to the aliphatic C—H

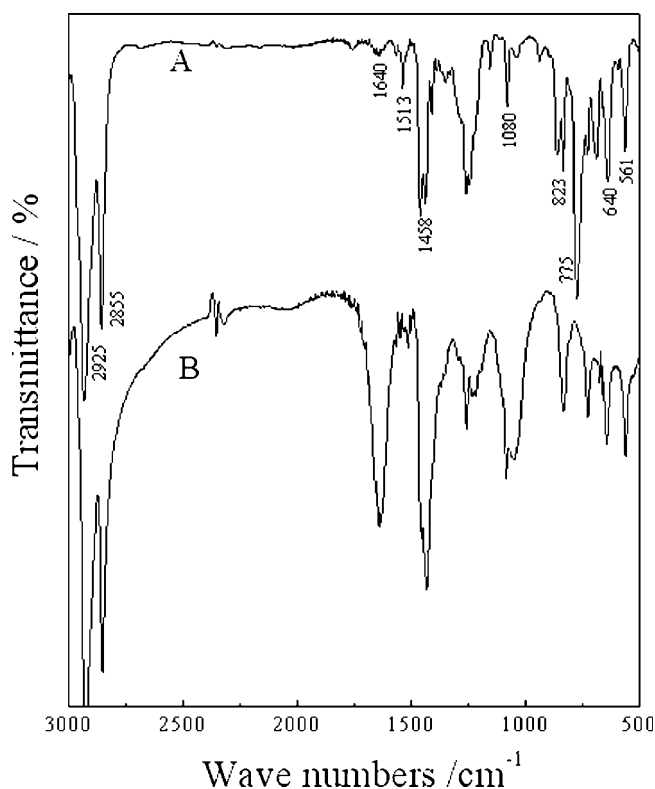
stretching vibration. The bands at 1513 and 1458  $\text{cm}^{-1}$  were the skeleton vibration of thiophene ring. The absorption of the aromatic C—C emerged at 1640  $\text{cm}^{-1}$ . The bands at 1080, 640 and 561  $\text{cm}^{-1}$  were the C—Br stretching vibration. Absorption vibration band at 823  $\text{cm}^{-1}$  were assigned to C $\beta$ —H out-of-plane deformation mode. The C $\alpha$ —H out-of-plane deformation vibration is at 775  $\text{cm}^{-1}$  [Fig. 5(A)].<sup>43,44</sup> After polymerization, the C $\alpha$ —H out-of-plane deformation vibration at 775  $\text{cm}^{-1}$  disappeared [Fig. 5(B)], confirming the polymerization of BHT at the  $\alpha$  position.

Figure 6A was the  $^1\text{H-NMR}$  spectrum of the monomer. There were eight groups of protons: 7.2456 (1H), 6.9380–6.9256 (2H), 3.4210–3.3892 (2H), 2.6539–2.6159 (2H), 1.8776–1.8416 (2H), 1.6404–1.6217 (2H), 1.4856–1.4500 (2H), and 1.3769–1.3594 (2H). The assignments of the NMR were shown in the insert of this spectrum. Figure 6B presented the  $^1\text{H-NMR}$  spectrum of PBHT. Due to its little solubility in  $\text{CDCl}_3$ , the chemical shifts of PBHT were much lower than those of  $\text{CDCl}_3$  at 7.2654 and  $\text{H}_2\text{O}$  at

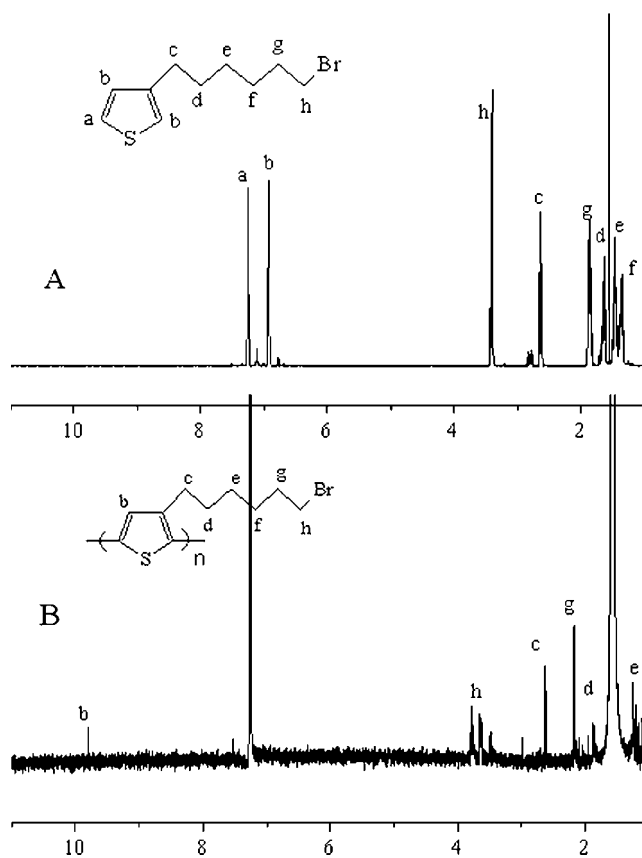


**Figure 4** UV-visible spectra of BHT monomer (insert) and doped PBHT films. The polymer films were electrodeposited from BFEE solution on ITO electrode containing 0.05 M BHT at a constant potential of 1.43 V.

1.5678. The PBHT spectrum showed only seven groups of protons, and the  $\alpha$ -H protons of thiophene ring have been eliminated due to the ring coupling reaction that occurred during the polymerization process. The chemical shift of  $\beta$ -H moved to much lower fields at 9.8023 than that of monomer at

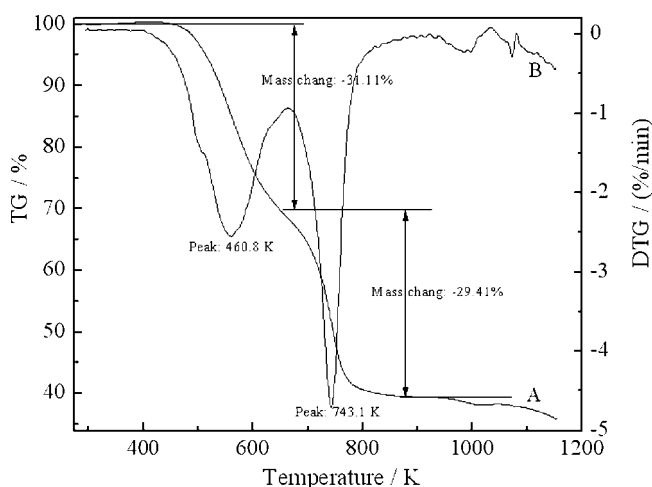


**Figure 5** Infrared spectra of BHT monomer (A) and dedoped PBHT films (B) prepared at 1.43 V from BFEE solution containing 0.05 M BHT.

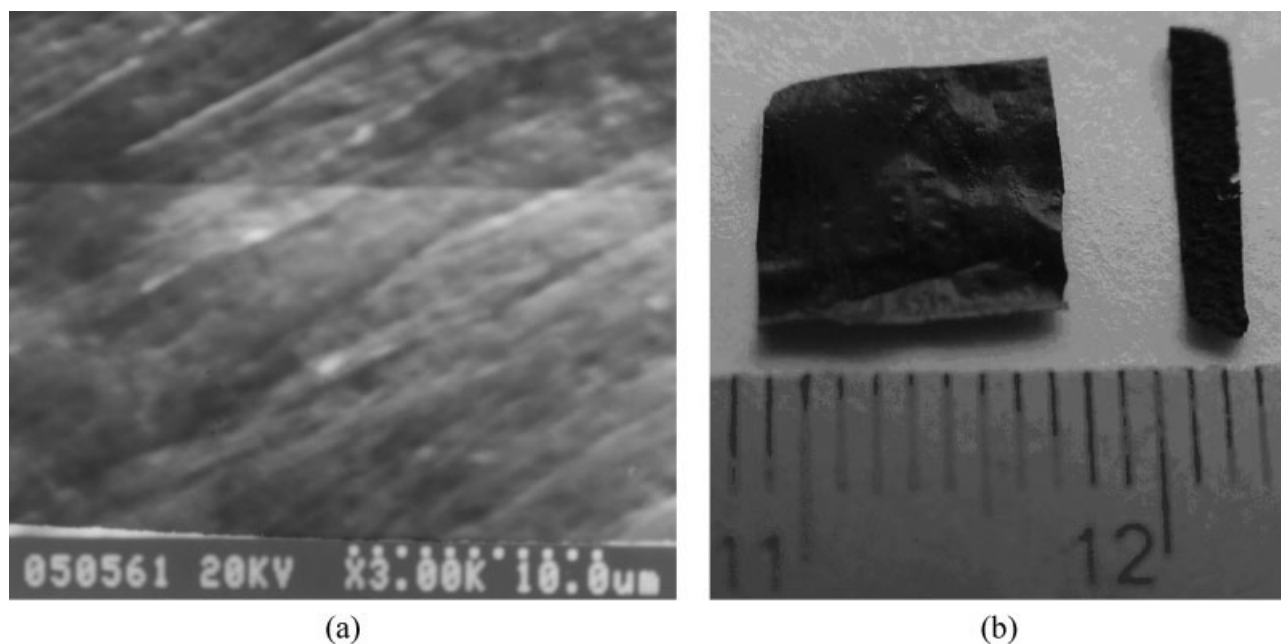


**Figure 6**  $^1\text{H-NMR}$  spectra of BHT (A) and dedoped PBHT (B). Solvent:  $\text{CDCl}_3$ .

7.2456. The extension of conjugation length of conjugated polymers usually led to the chemical shifts move to lower field.<sup>45</sup> Therefore, the shifts of  $\text{C}\beta\text{-H}$  of PBHT to lower fields further confirmed the formation of a conjugated delocalization structure. The protons of 6-bromohexyl remained unchanged, indicating that long chain was very stable during the



**Figure 7** TGA curve of dedoped PBHT films potentiostatically prepared at 1.43 V from BFEE solution containing 0.05 M BHT.



**Figure 8** (A) Scanning electron microscopy of doped PBHT film deposited on the electrode surface from BFEE. (B) Photograph of the PBHT film and fibers.

electrochemical polymerization. These results implied that the terminal bromine atom is very stable during the electrochemical polymerization of BHT.

#### Thermal analysis

The thermal stability of conducting polymers is very important for their potential application. Therefore, the thermal analysis of PBHT was determined by thermogravimetric analysis as shown in Figure 7. The thermal analysis was performed under a nitrogen stream in the temperature range of 293–1158 K with a heating rate of 10 K/min. As can be seen in Figure 7(A), the first weight loss occurred from 460 K to 660 K, up to 31.11%. This degradation may be ascribed to the decomposition of the Br atom from terminal long chain, which is satisfied with the theoretical value at 37.56%. The second decomposition up to 29.41% occurred between 660 K and 850 K. This weight loss can be attributed to the degradation of the skeletal PBHT backbone chain structure. From Figure 7B, in the temperature range of 460.8 and 743 K, the decomposition rate of PBHT films was fastest. These results indicated that thermal stability of PBHT films obtained from BFEE was fairly good.

#### Conductivity and morphology

The conductivity of the PBHT film obtained from BFEE was measured to be 20 S/cm, which is much lower than that of poly(3-methylthiophene) (80 S/cm)<sup>28</sup> and higher than that of poly(3-chlorothiophene)

(0.1 S/cm).<sup>31</sup> The PBHT film deposited on the electrode surface was homogeneous and smooth as confirmed by its scanning electron microscopy images [Fig. 8(A)]. In addition, the polymer film is flexible and has a fairly good mechanical strength. It can be peeled off from the electrode surface as a freestanding film and can be cut into various desired structures with a knife or a pair scissors [Fig. 8(B)]. It should be noted that the larger anode used for the electrochemical synthesis of PBHT in a large scale was a stainless steel sheet instead of the platinum electrode used for cyclic voltammetric measurements. The size of the polymer films were controlled by the electrode size and larger polymer films could be prepared when larger anode was used.

### CONCLUSIONS

High-quality freestanding PBHT films with conductivity of 20 S/cm were electrochemically synthesized in BFEE. The film prepared from these conditions was shiny and very flexible. It can be easily cut into any shapes with conventional mechanical methods. In addition, the polymer film showed good redox activity and good thermal stability property. As formed polymer films were also characterized by FT-IR, UV-visible, <sup>1</sup>H-NMR spectroscopy, SEM. Doped PBHT was insoluble in all organic solvent and dedoped PBHT can be dissolved very little in THF, DMSO, etc. The terminal bromine atom does not have a negative effect on the electropolymerization of BHT.

## References

1. Goldenberg, L. M.; Lacaze, P. C. *Synth Met* 1993, 58, 271.
2. Li, C.; Shi, G.; Liang, Y.; Ye, W.; Sha, Z. *Polymer* 1997, 38, 5023.
3. Qiu, H. J.; Wan, M. X.; Matthew, B.; Dai, L. M. *Macromolecules* 2001, 34, 675.
4. Xu, J.; Shi, G.; Qu, L.; Zhang, J. *Synth Met* 2003, 135–136, 221.
5. Wan, X.; Liu, X.; Xue, G.; Jiang, L.; Hao, J. *Polymer* 1999, 40, 4907.
6. Otero, T. F.; Rodriguez, J. *J Electroanal Chem* 1994, 379, 513.
7. Waltman, R. J.; Bargon, J.; Diaz, A. F. *J Phys Chem* 1983, 87, 1459.
8. Roncali, J. *Chem Rev* 1992, 92, 711.
9. Chan, H. S. O.; Choon, S. C. *Prog Polym Eng Sci* 1998, 23, 1167.
10. Sankaran, B.; Reynolds, J. R. *Macromolecules* 1997, 30, 2582.
11. Bazaour, E. A.; Aeiach, S.; Lacaze, P. C. *J Electroanal Chem* 1994, 364, 63.
12. Gurunathan, K.; Murugan, A. V.; Marimuthu, R. *Mater Chem Phys* 1999, 61, 173.
13. Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *Macromolecules* 1993, 26, 4094.
14. Feast, W. J.; Tsibouklis, J.; Pouwer, K. L. *Polymer* 1996, 22, 5017.
15. Pu, S.; Hou, J.; Xu, J.; Nie, G.; Zhang S.; Shen, L.; Xiao, Q. *Mater Lett* 2005, 59, 1061.
16. Groenendaal, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Adv Mater* 2003, 11, 855.
17. Shi, G.; Jin, S.; Xue, G.; Li, C. *Science* 1995, 267, 994.
18. Li, C.; Shi, G.; Xue, G.; Jin, S.; Yu, B.; Yang, S. *J Polym Sci B* 1995, 33, 2199.
19. Jin, S.; Ji, M.; Xue, G. *Appl Phys A* 1996, 63, 397.
20. Zhou, L.; Li, Y.; Xue G. *Thin Solid Films* 1998, 335, 112.
21. Vardhanan, R. V.; Zhou, L.; Gao, Z. *Thin Solid Films* 1999, 35, 283.
22. Shi, G.; Li, C.; Liang, Y. *Adv Mater* 1999, 11, 1145.
23. Li, X.; Li, Y. *J Appl Polym Sci* 2003, 90, 940.
24. Alkan, S.; Cutler, C. A.; Reynolds, J. R. *Adv Funct Mater* 2003, 13, 331.
25. Cao, J.; Sun, J.; Shi, G.; Chen, H.; Zhang, Q.; Wang, D.; Wang, M. *Mater Chem Phys* 2003, 82, 44.
26. Qiao, X.; Wang, X.; Mo, Z. *Synth Met* 2001, 118, 89.
27. Zhang, Z.; Shi, G.; Wu, X.; Qu, L. *Acta Polym Sin* 2004, 1, 140.
28. Zhou, L.; Jin, S.; Xue, G. *Macromol Chem Phys* 1996, 197, 3309.
29. Zhou L.; Xue, G. *Synth Met* 1997, 87, 193.
30. Xu, J.; Shi, G.; Chen, F.; Wang, F.; Zhang, J.; Hong, X. *J Appl Polym Sci* 2003, 87, 502.
31. Xu, J.; Shi, G.; Xu, Z.; Chen, F.; Hong, X. *J Electroanal Chem* 2001, 514, 16.
32. Shen, L.; Xu, J.; Wei, Z.; Hou, J. *Eur Polym J* 2005, 41, 1738.
33. Kassmi, A. E.; Fache, F.; Lemaire, M. *J Electroanal Chem* 1994, 373, 241.
34. Groenendaal, L. B.; Jonas, F. *Adv Mater* 2000, 12, 481.
35. Heywang, G.; Jonas, F. *Adv Mater* 1992, 4, 116.
36. Kannan, R.; He, G.; Yuan, L.; Xu, F.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A. *Chem Mater* 2001, 13, 1896.
37. Brisset, H.; Navarro, A. E.; Moustrou, C.; Perepichka, I. F.; Roncali, J. *Electrochem Commun* 2004, 6, 249.
38. Kristoffer, K. S.; Heuze, K.; McCullough, R. D. *Macromolecules* 2003, 36, 7114.
39. Downard, A. J.; Pletcher, D. *J Electroanal Chem* 1987, 206, 147.
40. Li, C.; Shi, G.; Liang, Y. *Synth Met* 1999, 104, 113.
41. Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem Rev* 88, 1988, 183.
42. Chung, T. C.; Karfman, J. H.; Heeger, A. R.; Wudl, F. *Phys Rev B* 30, 1984, 702.
43. Furakawa, Y.; Akimoto, M.; Harada, I. *Synth Met* 1987, 18, 51.
44. Sauvajol, J. L.; Chenouini, D.; Lere-Porte, J. P.; Chorro, C.; Moukala, B.; Petrissans, J. *Synth Met* 1990, 38, 1.
45. Xu, J.; Zhou, W.; Chen, B.; Pu, S.; Wang, J.; Wan, Y. *J Polym Sci Part A: Polym Chem* 2006, 44, 1125.