Electrosyntheses and Characterization of Poly(5-bromoindole) in Boron Trifluoride Diethyl Etherate

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ABSTRACT: Poly(5-bromoindole) (PBrI) films were synthesized electrochemically by direct oxidation of 5-bromoindole in pure boron trifluoride diethyl etherate. The oxidation potential of 5-bromoindole in this medium was measured to be only 0.97 V *vs.* saturated calomel electrode, which was lower than that determined in acetonitrile + 0.1 mol L^{-1} Bu$_4$NBF$_4$ (1.08 V). PBrI films obtained from this medium showed good electrochemical behavior and good thermal stability. Structural studies showed that the polymerization of 5-bromoindole ring occurred at 2,3 position. As-formed PBrI films were thoroughly soluble in strong polar solvent dimethylsulfoxide and partly soluble in tetrahydrofuran. Fluorescent spectral studies indicated that PBrI was a good blue-light emitter. The excitation and emission spectra of PBrI showed a significant shift to longer wavelength compared with that of the monomer, consistent with the greater extent of electron delocalization. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 539–547, 2006

Key words: electrochemical polymerization; conducting polymer; poly(5-bromoindole); boron trifluoride diethyl etherate; fluorescence

INTRODUCTION

In the past 25 years, inherently conducting polymers, such as poly(*p*-phenylene),[1,2] polyaniline,[3] polythiophene,[4–6] polypyrrole,[7–10] etc., have attracted great attention because of the wide fundamental interest and their potential industrial applications. Among them, polypyrrole has the advantages of good electrical conductivity, environmental stability, and ease of anodic electrodeposition of freestanding polypyrrole films. On the other hand, poly(*p*-phenylene) has the advantage of good thermal stability. Indole has both benzene ring and pyrrole ring. Thus polyindole may own the properties of both poly(*p*-phenylene) and polypyrrole together. Interest in the electrochemical polymerization of indole is due to its close structural similarities with pyrrole. Many statements about polyindole structure and polymerization mechanism were translated from polypyrrole studies. Therefore, polyindole and its derivatives had received a significant share of attention in the past few years[11–37] and may be a good candidate for applications in various domains like electronics, electrocatalysis, anode materials in battery, anticorrosion coatings, pharmacology, fast response potentiometric sensors, mild steel protection,[38] and for the direct oxidation and reduction of biomolecules. For many of these applications, it is desirable to produce electroactive polyindole layers with a wide variety of substitutent. One of the most widely used methods for achieving this will be the direct electrooxidation of 5-substituted indole monomers.

Conducting films of polyindole and its derivatives were mainly synthesized through electrochemical oxidation, except some work[14,15] concerning direct chemical oxidation of indole by FeCl$_3$. Electrochemical polymerization had been proved to be one of the most useful approaches for conducting polymer synthesis, with several advantages. First, one-step conducting film can be formed on the working electrode. Second, the amount of polymer deposited on the electrode can be controlled by the integrated charge passed through the cell. Third, only small amounts of monomer are required. Last, electrochemical studies can give fast information on the characteristics and properties of electropolymerized materials with good accuracy and precision.[39] Electrosynthesized polyindole and its derivative films had the advantages of fairly good thermal stability,[15–17] high redox activity and stability,[18]

slow degradation rate in comparison with that of polyaniline and polypyrrole,[17] and an air stable electrical conductivity close to 0.1 S cm^{-1} in the doped state.[19] The electrodeposition of polyindole and its derivatives was mainly performed in neutral solvents, such as acetonitrile[14,20,22] and CH$_2$Cl$_2$,[16] using ClO$_4^-$ or BF$_4^-$ as the supporting electrolyte. The main disadvantage of these media was that the properties of polyindole and its derivative films from these media were not very good, which are usually in the form of a powder. There were very few studies on the structural characterization of as-prepared polyindoles films because of the poor film quality. Therefore, it is very necessary to improve the quality of polyindole and its derivatives.

It is well known that free-standing films of polythiophene and its derivatives,[40,41] poly(p-phenylene)[42–44] and polypyrrole,[8] can be produced by direct anodic oxidation of corresponding monomers in boron trifluoride diethyl etherate (BFEE) with good mechanical, electrical, and thermal properties. The interactions between the middle strong Lewis acid, BFEE, and the aromatic monomers lower their oxidation potentials, and the catalytic effect of BFEE facilitates the formation of high quality free-standing polythiophene[45] and poly(p-phenylene) films. The mean conjugation length of polythiophene films prepared from pure BFEE was about 80 in comparison with that of 40 from acetonitrile.[46] Under these circumstances, BFEE serves not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte is needed. The ionic conductivity of freshly distilled BFEE may be as high as 400 μS cm^{-1}.[47] Recently, investigations on the electrochemical polymerization of fused ring compound, such as thianaphthene,[48] naphthalene,[49] naphthalenesulfonic acid,[50] etc., in BFEE, also proved the improvement of property in the corresponding conducting polymers. Moreover, the direct anodic oxidation of indole led to the formation of high quality conducting polyindole films on stainless steel sheet.[51]

The electropolymerization of 5-bromoindole was more difficult in neutral solvent because of the electron-withdrawing group substitution (bromine) on indole ring when comparedwith that of indole. Moreover, there were very little reports on the electropolymerization of 5-bromoindole.[52,53] The interest in this monomer was due to its further modification by other functional groups, through the reactions of bromine atom on the 5-position of indole. Therefore, it is very necessary to investigate the electrochemical polymerization of 5-bromoindole in BFEE.

In this paper, high quality poly(5-bromoindole) (PBrI) films can be easily prepared by anodic oxidation of 5-bromoindole monomer directly in pure BFEE. The electrochemical properties, morphology, and thermal stability of as-prepared PBrI films were studied. Its structure and polymerization mechanism were determined by FTIR, ^{1}H-NMR and UV-visible and fluorescent spectra.

EXPERIMENTAL

Materials

BFEE (Beijing Changyang Chemical Plant) was distilled and stored at $-20°C$ before use. 5-Bromoindole (Pingyuan Yongheng Dyestuff Chemical Company, Shangdong, China; analytical grade) and tetrabutylammonium tetrafluoroborate (TBATFB, 95%; Acros Organics,) was dried in vacuum at 60°C for 24 h before use. Commercial high performance liquid chromatography grade acetonitrile (ACN, Tianjin Siyou Bio-Fine Chemical Research Institute, Tianjin, China) was used directly without further purification. Ammonia (25%), prepared by Nanchang Hongdou Chemical Reagent Plant (Nanchang, China), was used as received. Dimethyl sulfoxide (DMSO; analytical grade) was from Tianjin Bodi Chemical Company (Tianjin, China). Deuterium-substituted dimethyl sulfoxide (CD$_3$SOCD$_3$) was a product of Beijing Chemical Plant (Beijing, China).

Electrosyntheses of PBrI films

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a CHI 660B potentiostat-galvanostat (Shanghai Chenhua Instrumental Cooperation Ltd., China) under computer control. The working and counter electrodes for cyclic voltammetry experiments were platinum wires with a diameter of 0.5 mm and stainless steel wires with a diameter of 1.5 mm, placed 0.5 cm apart, respectively. 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 the working and counter electrodes, respectively. Electrodes mentioned above were carefully polished with abrasive paper (1500 mesh), and cleaned with water and acetone successively, before each examination. All potentials were referred to a saturated calomel electrode (SCE).

The typical electrolytic solution was pure BFEE containing 0.05 mol L^{-1} 5-bromoindole. All solutions were deaerated by a dry nitrogen stream and maintained at a slight nitrogen 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 acetone. As-formed PBrI film was in doped state and dark green in color. For spectral analysis, the polymer was dedoped with 25% ammonia for 3 days and then washed repeatedly with water. Finally, it was dried under vacuum at 60°C for 2 days.
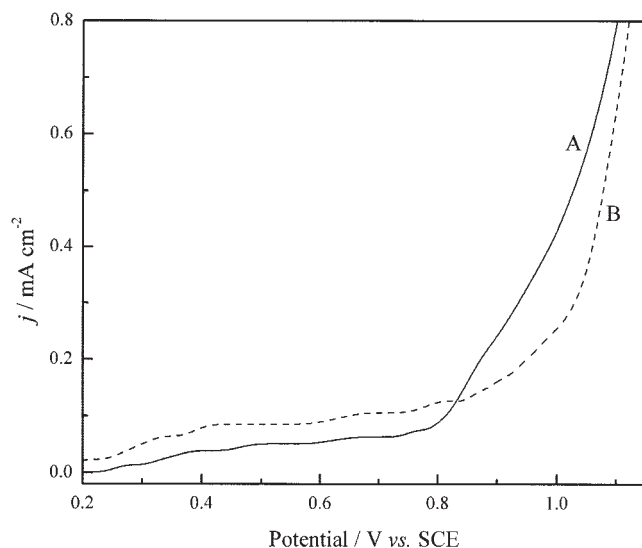
Figure 1 Anodic polarization curves of 5-bromoindole in BFEE (A) and in ACN + 0.1 mol L^{-1} TBATFB (B). Potential scan rates: 100 mV s^{-1}.

Characterizations

The conductivity of as-formed PBrI film was measured by conventional four-probe technique. UV-visible spectra were recorded using Perkin–Elmer Lambda 900 UV-Vis-NIR spectrophotometer. Infrared spectra were recorded using Nicolet 510P FT-IR spectrometer, with KBr pellets. The fluorescence spectra were determined with F-4500 fluorescence spectrophotometer (Hitachi). The ^{1}H-NMR spectrum was re-corded on a Bruker AV 400 nuclear magnetic resonance (NMR) spectrometer and CD_3SOCD_3 was used as the solvent. The thermogravimetric analysis (TGA) was performed with a thermal analyzer of Netzsch TG209. Scanning electron microscopy (SEM) measurements were taken using a JEOL JSM-6700F scanning electron microscope.

RESULTS AND DISCUSSION

Electrochemical syntheses of PBrI films

Figure 1 shows the anodic polarization curves of 5-bromoindole in pure BFEE (A) and in ACN containing 0.1 mol L^{-1} TBATFB (B). The oxidation onset of 5-bromoindole was initiated at 0.97 V *vs.* SCE in pure BFEE, which was lower than that of 5-bromoindole in ACN containing 0.1 mol L^{-1} TBATFB (1.08 V *vs.* SCE). This implies that the oxidation of 5-bromoindole in BFEE was easier than that in ACN/TBATFB. It should be noted here that BFEE is electrochemically silent in the whole potential range.[40]

The successive cyclic voltammograms (CVs) of 0.05 mol L^{-1} 5-bromoindole in pure BFEE on a platinum wire electrode is shown in Figure 2(A). As it can be seen from this figure, the CVs of 5-bromoindole in BFEE showed characteristic features as other conducting polymers such as polythiophene and polypyrrole, during potentiodynamic syntheses. As the CV scan continues, a polymer film is also formed on the working electrode surface. In BFEE, PBrI can be reduced and oxidized between 0.4 and 0.8 V versus SCE (Fig.
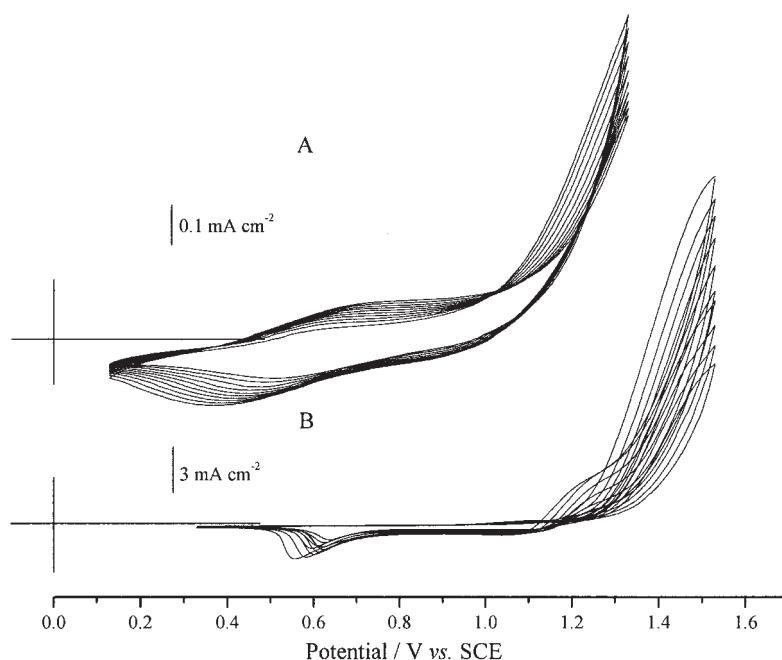

Figure 2 Cyclic voltammograms of 0.05 mol L^{-1} 5-bromoindole in pure BFEE (A) and in ACN + 0.1 mol L^{-1} TBATFB (B). Potential scan rates: 50 mV s^{-1}.

2(A)). The increase in the redox wave currents implied that the amount of the polymer on the electrode was increasing. The broad redox waves of as-formed PBrI film may be ascribable to the wide distribution of the polymer chain length[54] or the conversion of conductive species on polymer main chain from the neutral state to polarons, from polarons to bipolarons, and finally from bipolarons to the metallic state.[55] All these phenomena indicated that a high-quality conducting PBrI film was formed on the working electrode.

On the other hand, the successive CVs of 5-bromoindole in ACN containing 0.1 mol L^{-1} TBATFB was not very successful, although a polymer film still can be formed on the working electrode (Fig. 2(B)). The anodic current waves decreased quickly with the increases of CV scan numbers. This is mainly due to the fact that a thin polymer film was formed on the electrode surface and its electrical conductivity was much lower than that of stainless steel electrode. No apparent redox waves of the polymer were found, indicating that only a trace amount of the polymer was formed. From this point of view, BFEE is better than ACN as the medium for electrosyntheses of conducting PBrI films.

Electrochemistry of PBrI films

The electrochemical behavior of the PBrI films deposited electrochemically from pure BFEE was studied in monomer-free pure BFEE (Fig. 3(A)) and ACN containing 0.1 mol L^{-1} TBATFB (Fig. 3(B)), respectively. Similar to the results in the literature,[16] the steady-state cyclic voltammograms represented broad anodic and cathodic peaks. The peak current densities were both proportional to the scan rates (Figs. 3(A) and 3(B), insert), indicating the reversible redox behavior of the polymer. Furthermore, the anodic and cathodic peak potentials of these films were independent on the scan rates, suggesting that these redox reactions were both reversible. These films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials, indicating high stability of the polymer. According to Figure 3(A), the polymer film obtained from pure BFEE can be oxidized and reduced from 0.61 (E_a) to 0.52 V (E_c). The difference of (E_a-E_c) related to the kinetics of the doping and dedoping reactions, which was equal to 0.09 V for PBrI, implying good redox properties. The electrochemical behavior of PBrI in ACN + 0.1 mol L^{-1} TBATFB was similar to those of PBrI in pure BFEE, except higher potentials were needed to oxidize or reduce the polymer (E_a = 0.96 V, E_c = 0.92 V). The difference of (E_a-E_c), which was equal to about 0.04 V, was even lower than that in pure BFEE. The lower the difference of the anodic and cathodic potential, the more reversible is the redox reactions of the polymer. When a redox
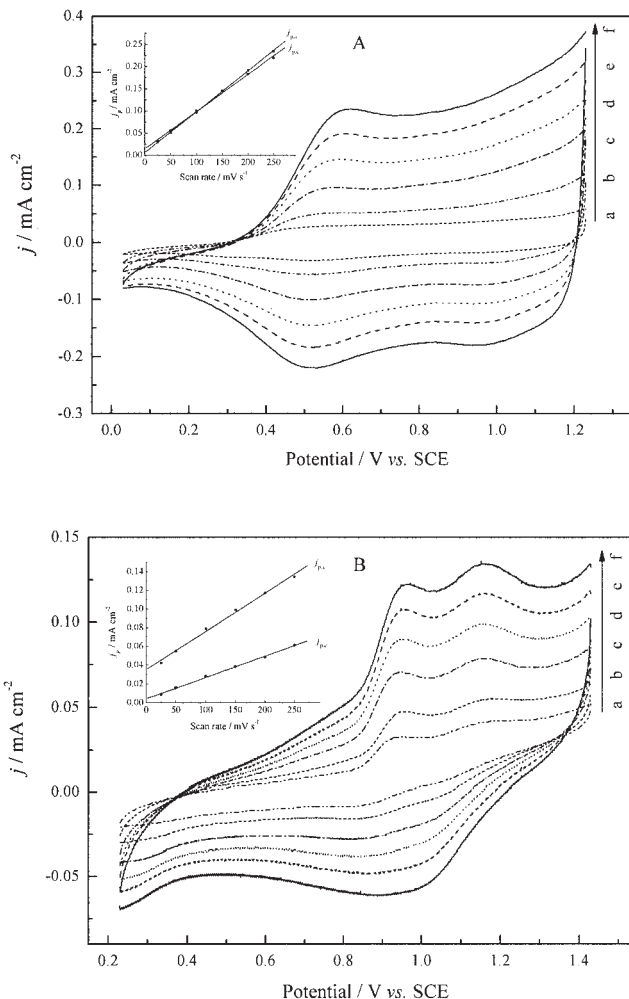

Figure 3 Cyclic voltammograms of PBrI films in monomer-free pure BFEE (A) and in ACN + 0.1 mol L^{-1} TBATFB (B) at potential scan rates of 25 mV s^{-1}(a), 50 mV s^{-1}(b), 100 mV s^{-1}(c), 150 mV s^{-1}(d), 200 mV s^{-1}(e), and 150 mV s^{-1}(f). The polymer film was synthesized electrochemically in BFEE at a constant applied potential of 1.13 V versus SCE, respectively.

reaction is really reversible, this difference will be equal to 0.0591/n, where n is the electron numbers per reaction. In the cases of electrosyntheses of conducting polymers, n is usually estimated to be 2. Therefore, the difference of anodic and cathodic potentials of PBrI is nearly equal to the theoretical value of reversible reaction. Previous studies showed that substituted conducting polymers prepared from nonsymmetric monomers usually show broad redox waves in their CVs,[56] which can also be observed in Figures 3(A) and 3(B). This phenomenon can be ascribed to the presence of coupling defects distributed statically, which result in a series of energetically nonequivalent chain segments. Based on these discussions above, it can be reasonably concluded that the doping and dedoping reaction of PBrI was nearly reversible with good redox stability.

Spectral characterization

During the potentiostatistic process, the color of BFEE containing 5-bromoindole darkened with the applying potential. This indicated that soluble 5-bromoindole oligomers formed during anodic oxidation. With the polymerizing propagation, part soluble oligomers became insoluble and 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 dark. This decreased the current efficiency of 5-bromoindole polymerization. PBrI film is gray green in the dedoped state while it is dark green in the doped form. The UV-visible spectra of dedoped PBrI films obtained from pure BFEE are shown in Figure 4(B). For comparison, the UV-visible spectrum of the monomer was also included in Figure 4(A). 5-Bromoindole monomer shows several characteristic absorption at 274, 260, and 222 nm. On the contrary, the spectra of the dedoped PBrI films show a much broader absorption from 250 to about 420 nm. This implies the wide molar mass distribution of as-prepared PBrI films. Previous studies indicated that polyindoles with absorption lower than 410 nm were soluble in ACN.[21,37] This accounts for the solubility of PBrI film in the strong polar organic solvent, DMSO. However, PBrI film can not be dissolved in common organic solvents, such as acetonitrile, acetone, ethyl etherate, CH_2Cl_2, $CHCl_3$, hexane, methanol, ethanol, toluene, etc., and can only be partly dissovled in THF.

Vibrational spectra can provide structural information on neutral and doped conducting polymers, especially for those insoluble and infusible. The comparison on the evolution of the vibrational modes appearing in conducting polymers and in some simpler related molecules acting as references usually facili-
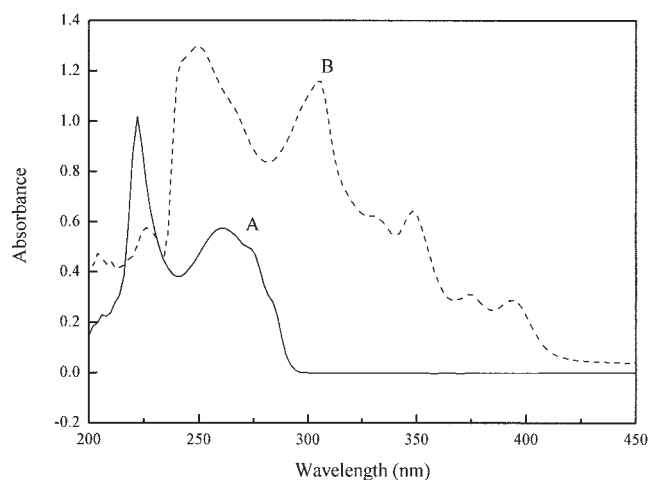

Figure 4 UV-visible spectra of 5-bromoindole monomer (A) and dedoped PBrI prepared from pure BFEE at a constant applied potential of 1.13 V versus SCE (B).
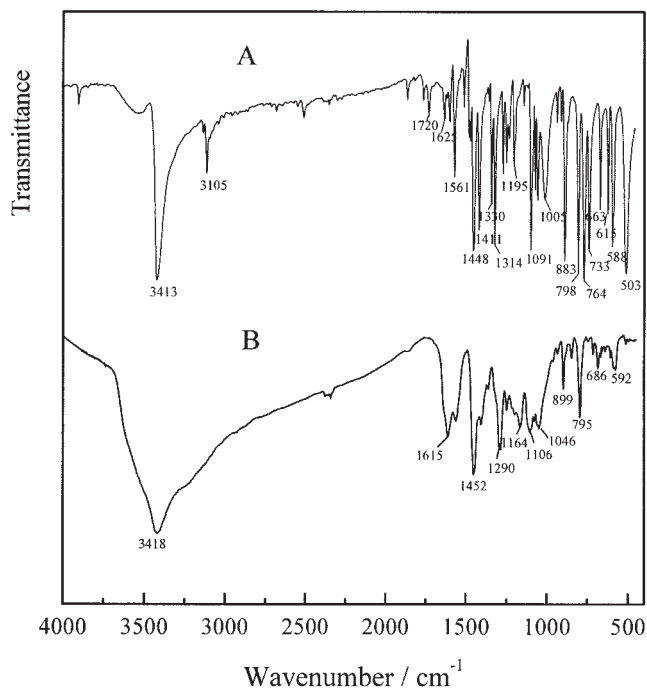

Figure 5 FTIR spectra of 5-bromoindole monomer (A), and PBrI films (B) obtained potentiostatically at 1.13 V versus SCE from pure BFEE after treatment with 25% aqueous ammonia for 3 days.

tates the interpretation of the experimental absorption spectra. For polyindole and its derivatives, vibrational spectra are also unique because they may interpret the debating of polymerization mechanism. From the literature, there were two main opinions on the electrochemical polymerization mechanism of indole, 1,3 position or 2,3 position. The presence or absence of N—H vibration mode in the spectrum of dedoped polyindoles is the key factor for determining the polymerization whether occurred at 1 position.

Figure 5 displays the transmittance FTIR spectra of the 5-bromoindole monomer (A) and the dedoped PBrI (B) obtained from pure BFEE. The strong and narrow peak at 3413 cm^{-1} in the 5-bromoindole spectrum (Fig. 5(A)) is the characteristic absorption of the N—H bond, which is broader and shifted to 3418 cm^{-1} in the spectrum of the dedoped PBrI film (Fig. 5(B)). This band, together with the bands at 1615, 1290, and 592 cm^{-1}, can be ascribed to the in-plane bending, stretching, and out-of-plane bending vibrations of the N—H bond, respectively.[57] This result implies that still there were N—H bonds on the dedoped PBrI backbone. Thus, nitrogen species could not be the polymerization sites, and polymerization should occur at the 2- and 3-positions. The single peak located at 1452 cm^{-1} (Fig. 5(B)) was assigned to the stretching of the benzene ring. The peak located at 795, 899 cm^{-1} and 1046, 1164 cm^{-1} can be assigned to the in-plane and the out-of-plane bending of the C—H bonds, respectively, (Fig. 5(B)).[57]
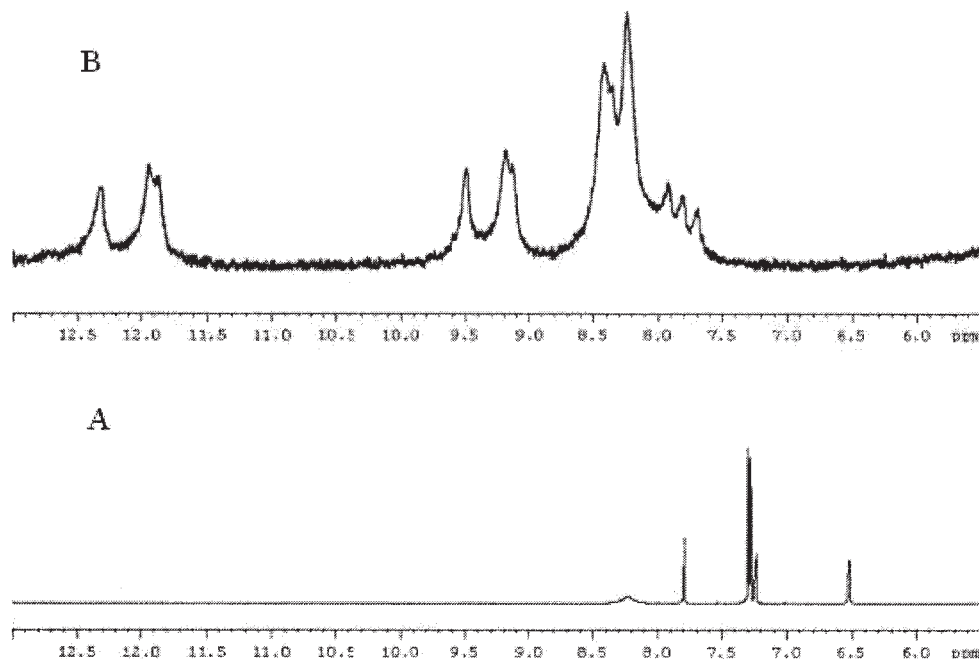
Figure 6 ^{1}H-NMR spectrum of 5-bromoindole (A) and dedoped PBrI prepared from BFEE (B). Solvent: CD$_3$SOCD$_3$.

To get deep insight into the polymer structure and the polymerization mechanism of 5-bromoindole, the ^{1}H-NMR spectra of the monomer and the dedoped PBrI obtained from pure BFEE were recorded, as illustrated in Figures 6(A) and 6(B), respectively. According to the literature,[58] the chemical shift of N—H bond in ^{1}H-NMR spectrum of indole is at 10.1, while that of pyrrole is at around 8.0. The incorporation of benzene ring onto pyrrole ring made the chemical shift of N—H bond move to lower field. Therefore, it can be reasonably deduced that by introducing higher conjugation length onto the PBrI main chain, the chemical shift of N—H bond can move to lower field further. However, the introduction of bromine substitution at 5 position leads to the down shift of the chemical shift of N—H bond, which is at 8.2 as shown in Figure 6(A). As illustrated in Figure 6(B), the spectrum of PBrI showed four groups of protons: ~7.8, 8.3, 9.3, and 12.0. These proton lines were much broader than the corresponding proton lines of the monomer because of the wide molar mass distribution of PBrI. Based on these considerations, the chemical shift of 12.0 in Figure 6(B) can be assigned to the N—H bond in PBrI, which means that the N—H bond is still present on the main chain of the polymer, in accordance with the FTIR results. The existence of N—H bond further by ^{1}H-NMR in as-formed PBrI films proved the electropolymerization mechanism of 5-bromoindole at 2,3 position. The peaks between δ 9.0 and 9.4 arise from the proton in the 4-position of the benzene ring on one of the indole units. The groups of peaks at lower chemical shifts, around δ 8.0, arise from

the protons in the 6- and 7-positions of the benzene rings. Confirmation of these assignments is found by integrating the peaks, which shows that the peaks around δ12, 9, and 8 arise from nearly one, one and two protons, respectively.

Much interest has been directed toward the fluorescence properties of indole and its derivatives, as it is the fluorophore of the amino acid tryptophan, which was used extensively as a fluorescent probe in the studies of protein and enzyme structure. The fluorescence properties of indoles are very sensitive to environmental conditions, as an unusually large Stokes shift is observed in polar media.[59] This shift arises from a bathochromic shift in the emission wavelength with increasing solvent polarity. The energy of the absorption band displays a much lower solvent dependence.[59] Previous studies indicated that the presence of both electron withdrawing and electron donating groups result in a bathochromic shift of the emission maxima relative to unsubstituted indole. Although the fluorescence of 5-bromine substituted indole can be detected in the literature,[59] in our experiment its fluorescence was very weak under the same conditions in comparison with PBrI. Because PBrI can only be dissolved in DMSO, therefore, the fluorescence of dedoped PBrI was only examined using DMSO as the solvent using steady state fluorescence spectroscopy in solution at room temperature through the 3-D scans of excitation-emission-intensity, as shown in Figure 7. According to Figure 7, the obvious peaks of excitation spectra can be found at 300, 350, and 408 nm, while the emission spectra have several
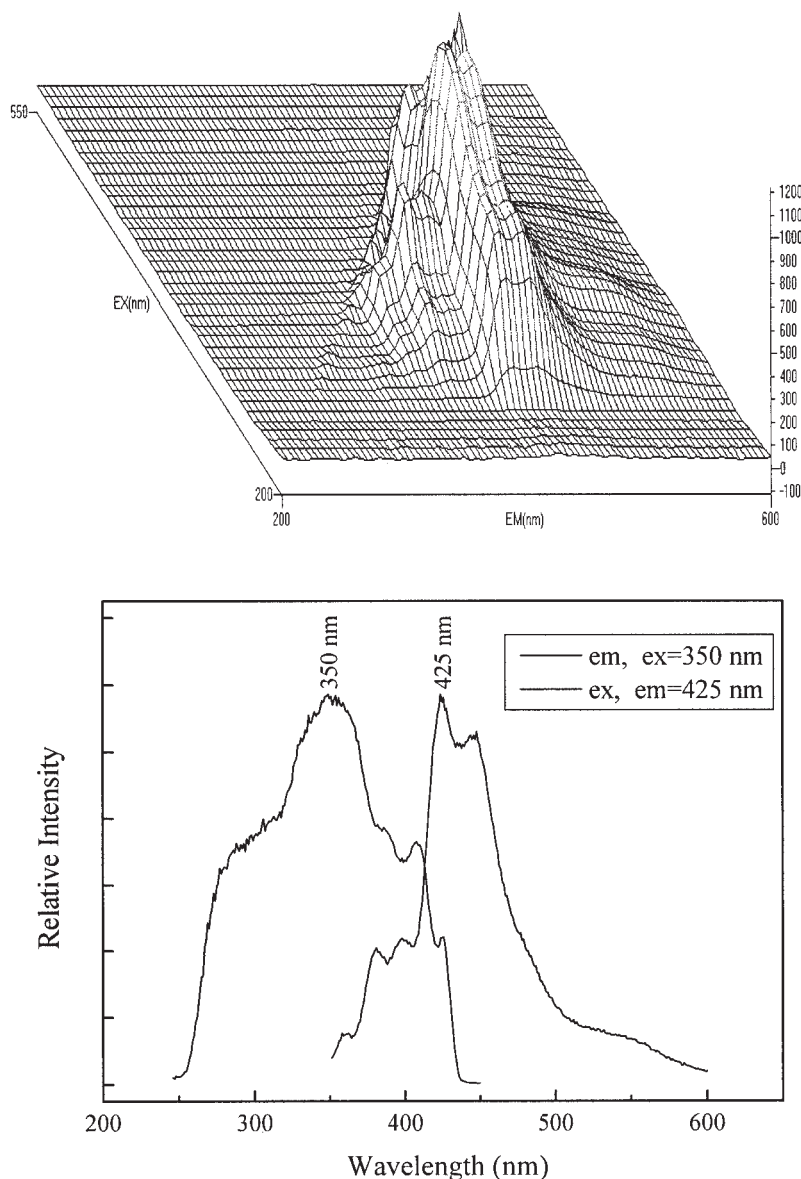
Figure 7 The 3D fluorescence scans of emission (EM)-excitation (EX)-intensity of dedoped PBrI prepared from BFEE (A), *X*-axis: emission wavelength, *Y*-axis: excitation wavelength, *Z*-axis: relative intensity. The excitation (EM = 425 nm) and the emission (EX = 350 nm) spectra of dedoped PBrI (B). Solvent: DMSO.

peaks mainly at 398, 425, and 445 nm. The wide peak distribution can be ascribed to the wide molar mass distribution of PBrI, in accordance with UV-visible spectra and ^{1}H-NMR results. The excitation and emission spectra of PBrI showed a significant shift to longer wavelength compared to the monomer, consistent with the greater extent of electron delocalization. The blue shift of the excitation and emission spectra of PBrI in comparison with polyindole (excitation peaks 400, 410, and 430 nm, emission peaks 425, 435, and 460 nm) implies that the substitution of heavy atom bromine at 5 position may have negative influence on electrosynthesized PBrI films. These results described above indicated that the polymer is a good blue light emitter and also denotes that PBrI may have some

potential application in various fields, such as the field of organic laser.

Thermal analysis

The thermal stability of conducting polymers is very important for their potential use. TGA is a significant dynamic way of detecting degradation behaviors. The weight loss of a polymer sample is measured continuously, whereas the temperature is changed at a constant rate. To investigate the thermal stability of PBrI films prepared in BFEE, the thermal analyses of dedoped PBrI films were tested as shown in Figure 8. The thermal analysis was performed under a nitrogen

stream in the temperature range of 280–1260 K at a heating rate of 10 K min^{-1}. Before 603 K, the weight losses of the polymer were about 10% (Fig. 8), possibly due to the evaporation of trace water or other moisture trapped in the polymer.[60] For temperatures higher than 603 K, as shown in Figure 8, there was evident weight loss from 603 to 873 K, up to 45%. This prominent weight loss was attributed to the degradation of the skeletal PBrI backbone chain structure. In addition, there was still decomposition between 900 and 1260 K, as shown in Figure 8, possibly because of the overflow of bromine substituted part of decomposed PBrI.

Morphology and conductivity

The conductivity of the PBrI film obtained from pure BFEE was measured to be 10^{-2} S cm^{-1}, using conventional four-probe technique. The SEM image of a PBrI film was shown in Figure 9. The morphology analysis showed that the polymer film resembled ordered arrangements of granules. The growth of the nuclei was in the form of clusters. This morphology facilitated the movement of doping anions into and out of the polymer film during doping and dedoping, in agreement with the high redox activity of PBrI films in BFEE and ACN containing 0.1 mol L^{-1} TBATFB (Fig. 3). This also confirmed the high quality PBrI prepared in BFEE.

CONCLUSIONS

PBrI films with a conductivity of 10^{-2} S cm^{-1} were electrochemically synthesized in pure BFEE containing 0.05 mol L^{-1} 5-bromoindole monomer. The oxida-
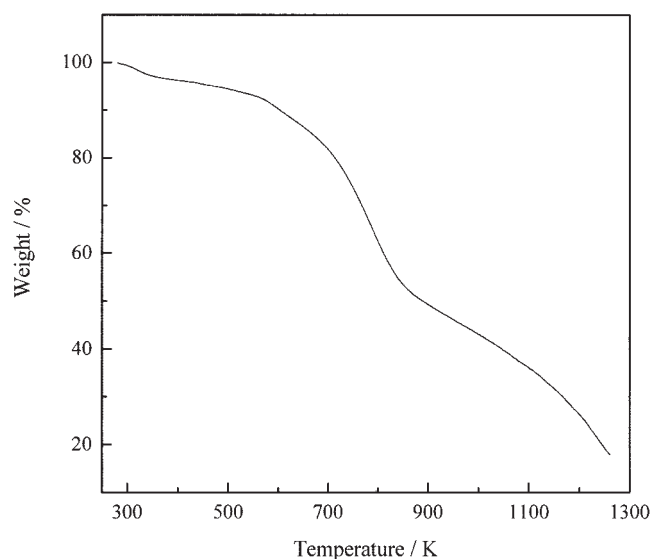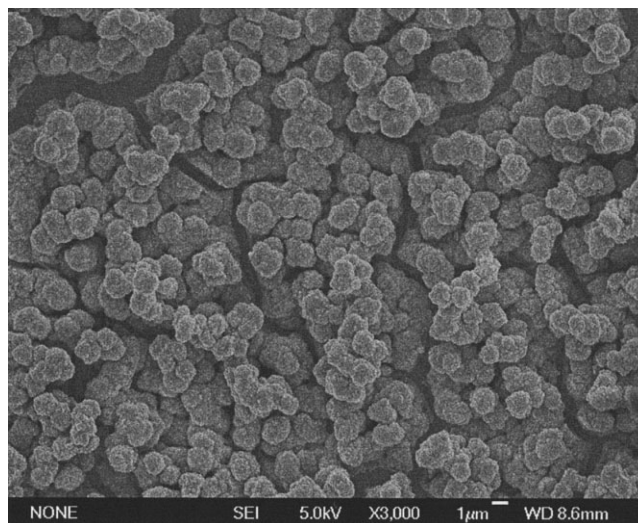

Figure 9 Scanning electron micrographs of PBrI film deposited on the electrode surface from pure BFEE, at a constant applied potential of 1.13 V versus SCE.

tion potential of 5-bromoindole in this medium was determined to be only 0.97 V *vs.* SCE, which was lower than that in ACN (1.08 V *vs.* SCE). As-formed PBrI films showed good redox activity. Electrochemical studies indicated that BFEE was a better medium than ACN for the syntheses of PBrI. According to IR and ^{1}H-NMR spectra, the existence of the N—H bond implied that coupling between the monomer units occurred at the C_2 and C_3 positions. TGA results indicated the good thermal stability of PBrI films. The fluorescence spectra suggested that soluble PBrI was a good blue-light emitter.

Figure 8 TGA curve of dedoped PBrI films obtained potentiostatically at 1.13 V versus SCE from pure BFEE.

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