

# Electrochemical Preparation of Polythiophene in Acetonitrile Solution with Boron Fluoride–Ethyl Ether as the Electrolyte

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**ABSTRACT:** Polythiophene (PTh) films were prepared by the electrochemical polymerization of thiophene in acetonitrile solution with boron fluoride–ethyl ether (BFEE) as the electrolyte. The electropolymerization processes were investigated by cyclic voltammetry. The onset potential of the electropolymerization decreased dramatically with increasing BFEE proportion in the solution. The free-standing PTh films obtained were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray photoelectron microscopy. The influence of BFEE on the morphology and conductivity of the PTh films was also

examined. The binary solvent solution consisted of acetonitrile (10 vol %) and BFEE (90 vol %), which turned out to be the optimal electrosynthesis system, in which a current density of 1 mA/cm<sup>2</sup> and a monomer concentration of 50 mM were the optimal conditions for electropolymerization. The PTh film obtained under the optimized conditions had a high tensile strength of 60 MPa and a high conductivity of 153 S/cm. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 940–946, 2003

**Key words:** conducting polymers

## INTRODUCTION

Studies on conducting polythiophene (PTh) have received more and more attention recently because of its promise for application in antistatic coating,<sup>1</sup> transparent electrode,<sup>2</sup> supercapacitors,<sup>3</sup> electrochromic display,<sup>4</sup> light-emitting diodes,<sup>5</sup> photovoltaic cells,<sup>6</sup> and polymer field-effect transistor (FET),<sup>7</sup> and so on. PTh can be synthesized by the chemical or electrochemical polymerization of thiophene. In comparison with chemical synthesis, the electrochemical preparation of PTh possesses many advantages, including its ability to produce free-standing PTh films directly on the electrodes and the ease of controlling the thickness of the films. Therefore, a large amount of research work has been devoted to the electrochemical preparation of PTh films, especially to the optimization of the electropolymerization conditions.<sup>8</sup>

The studies on these electropolymerization conditions have indicated that many factors, including the solvent (especially the presence or absence of water),<sup>9</sup>

temperature,<sup>10</sup> concentration of the monomer,<sup>11</sup> and supporting electrolyte,<sup>12</sup> affect the properties of the PTh films as they are prepared. PTh has been successfully deposited onto platinum from a concentrated solution of thiophene in acetonitrile.<sup>13</sup> In addition, the electrochemical properties of PTh films in acetonitrile were also studied intensively.<sup>14–17</sup> It was found that the supporting electrolyte, especially the anion type, has a strong effect on the electrochemical properties of the PTh films.

The potential of the oxidative polymerization of thiophene is usually over 1.7 V versus Ag/AgCl in an organic solution such as 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN solution.<sup>13</sup> The high potential makes the electropolymerization of thiophene quite difficult, and the PTh films produced on the electrode are easily overoxidized during further electropolymerization. Obviously, it is beneficial to the preparation of high-quality PTh films if the polymerization potential can be decreased. In 1995, Shi et al.<sup>18</sup> decreased the potential to about 1.0 V versus Ag/AgCl by performing the electropolymerization of thiophene in pure boron fluoride–ethylether (BFEE) solution. With the lower polymerization potential, they prepared flexible PTh films with strong mechanical properties. However, the mechanism of the influence of BFEE on the electropolymerization is still not very clear. In this study, BFEE was used as the supporting electrolyte in acetonitrile solution for the electrochemical preparation of PTh.

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The onset electropolymerization potential of thiophene decreased with increasing BFEE proportion. The PTh films obtained were shiny, flexible, and compact. The influence of BFEE and thiophene monomer concentration on the polymerization processes and on the properties of the as-prepared PTh films were also examined.

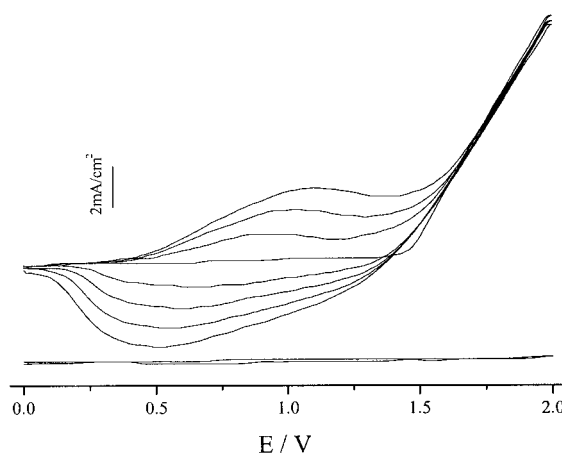
## EXPERIMENTAL

PTh deposition was performed by the cyclic voltammetric or galvanostatic method in a one-compartment cell with an EG&G model 283 potentiostat/galvanostat under computer control. Cyclic voltammetry experiments and galvanostatic experiments were performed with platinum as the working electrode and counterelectrode, respectively, and a silver wire as the reference electrode. To provide a more general reference, we examined the ferrocene-ferrocenium redox couple in a mixed solution containing acetonitrile and BFEE. Its half-wave potential  $[1/2(E_{pa} + E_{pc})]$ , where  $a$  is the anodic and  $c$  is the cathodic potentials, was found to be 0.079 V (vs Ag wire). Thus, a correction of 0.321 V ( $-0.079 + 0.400$ V) was needed to bring the measured potentials in binary solution versus silver wire to potentials versus the standard hydrogen electrode.<sup>19</sup> The electrolyte used for PTh deposition was an acetonitrile (Aldrich, without further purification) solution mixed with freshly distilled BFEE. It was deaerated by dry  $N_2$  bubbling, and the  $N_2$  stream was maintained at a light overpressure during the experiment. The current density applied in the galvanostatic electrosynthesis of the PTh films for conductivity measurements was controlled at  $1 \text{ mA/cm}^2$ . The as-prepared PTh films were finally rinsed by diethyl ether and dried *in vacuo* before characterization. The Fourier transform infrared (FTIR) spectra of PTh were recorded with a PE 2000 infrared spectrometer. Morphologies of the PTh films were observed with a HS-530 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was measured with an ESCA Lab 220I-XL X-ray photoelectron spectrometer. The film thickness was determined with an electronic outside micrometer (Qinghai, China). Direct-current conductivity and mechanical properties were measured by the conventional four-probe technique and an instron 1122 universal testing instrument at a stretching rate of  $0.5 \text{ cm/min}^{-1}$ , respectively.

## RESULTS AND DISCUSSION

### Electrosynthesis in acetonitrile solution with BFEE as the electrolyte

The oxidative polymerization process of thiophene on a platinum substrate was studied by cyclic voltammetry. Figure 1(A) shows the cyclic voltammograms in



**Figure 1** Cyclic voltammograms of (A)  $12 \text{ mmol L}^{-1}$  thiophene and an acetonitrile solution with 4% (v/v) BFEE and (B) an acetonitrile solution with 4% (v/v) BFEE without thiophene at a potential scan rate of  $30 \text{ mV/s}$  on a platinum sheet ( $1 \times 2 \text{ cm}$ ).

the acetonitrile solution containing  $12 \text{ mmol L}^{-1}$  thiophene and 4% BFEE (the proportion was by volume unless otherwise stated) in the potential range between 0.0 and 2.0 V. In the first cycle, the anodic current began to increase at 1.48 V, and there was a current loop between 1.48 and 2.0 V. The formation of this loop is characteristic of nucleation processes, as reported in the literature.<sup>15</sup> Also, the formation of a PTh film on the electrode was observed at potentials greater than 1.48 V. The redox peaks at 1.1 and 0.6 V were attributed to the  $p$ -doping/dedoping processes of the PTh film formed in previous potential scans. The increase of the redox current with increasing cycle number of the potential scan implied that the amount of the polymer on the electrode increased cycle by cycle. The CV of the acetonitrile solution containing BFEE without thiophene showed no current waves in the same potential range [see Fig. 1(B)], which demonstrated that the electrolyte and electrode were electrochemically inserted in the potential range.

The PTh film obtained from the acetonitrile solution with 4% BFEE was shiny, flexible, and compact. Figure 2 shows the FTIR spectrum of the PTh film dedoped with 5% ammonia aqueous solution. Those peaks at  $1491$  and  $1437 \text{ cm}^{-1}$  showed aromatic-ring stretching bands.<sup>20</sup> Those at  $841 \text{ cm}^{-1}$  (medium),  $785 \text{ cm}^{-1}$  (strong), and  $699 \text{ cm}^{-1}$  (weak) were attributed to C-H out-of-plane vibrations. The strong intensity of the  $785 \text{ cm}^{-1}$  band, which is characteristic of a 2,5-disubstituted thiophene ring, indicated that the electrochemical coupling of thiophene rings occurred preferentially at the 2,5 position (i.e.,  $\alpha$ - $\alpha$  linkage).<sup>20</sup> It is well documented that the  $\alpha$  position in the monomer is more reactive than the  $\beta$  position, and therefore, the  $\alpha$ - $\alpha$  linkages are predominant in the polymer chain.<sup>13</sup>

The XPS spectrum of doped PTh film deposited on the platinum substrate was also investigated.  $S_{2p}$ ,  $F_{1s}$ ,

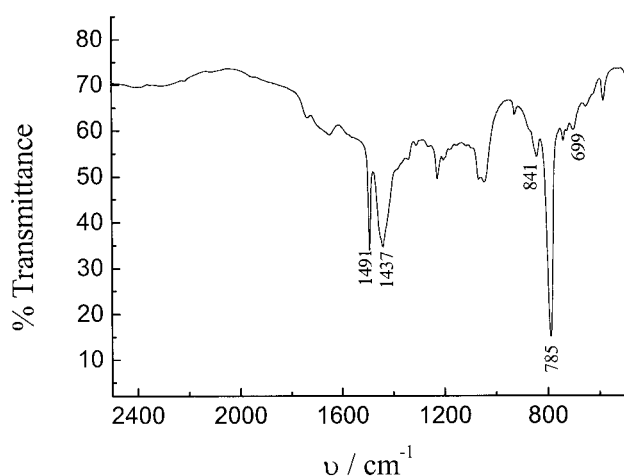
and  $B_{1s}$  were located at 163.5, 685.7, and 193.3 eV, respectively. The S : C atomic ratio calculated from the peak areas was 1:6. The B : F atomic ratio was about 1:3. Because boron trifluoride etherate exists in diethyl ether as a solvated ion-pair 1, or ethoxyonium fluoro-borate 2;<sup>21</sup>



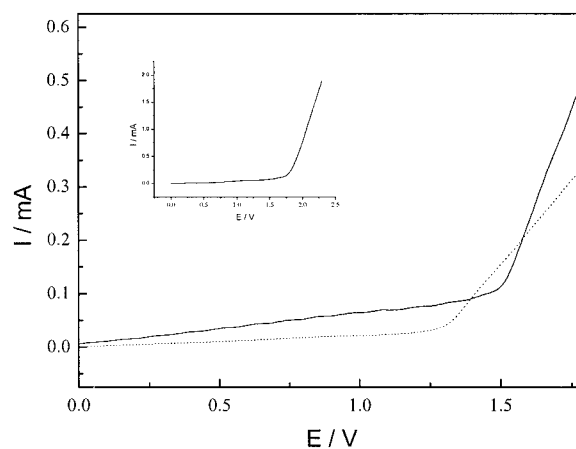
From the discussion, one can infer that the doped species may have been  $\text{BF}_3\text{OEt}^-$  and that BFEE may have existed in acetonitrile as  $\text{Et}_3\text{O}^+$  and  $\text{BF}_3\text{OEt}^-$ .

### Effect of BFEE concentration on electropolymerization

BFEE was first used as the supporting electrolyte in acetonitrile solutions without other salts for the electropolymerization of thiophene. When different volume proportions of BFEE were added to acetonitrile with 12 mmol  $\text{L}^{-1}$  thiophene, the onset potential of the electropolymerization of thiophene decreased with increasing BFEE concentration, as shown in Figure 3 and Table I. The onset potential decreased in the acetonitrile solution from 1.75 V without BFEE to 1.16 V with 95% BFEE. The potential decrease in the acetonitrile solution with BFEE could be attributed to the catalytic effect of the Lewis acid on the deprotonation of thiophene on the electrode.<sup>18</sup> The lower oxidation potential of thiophene in those systems may have diminished the content of  $\alpha$ - $\beta'$  linkages between monomer units, thereby imparting a greater linearity to the overall structure of PTh which should have resulted in improved stereoregularity. Meanwhile, BFEE existed as polar molecular  $\text{Et}_3\text{O}^+$  and  $\text{BF}_3\text{OEt}^-$ , which supported the conducting medium. On the basis of these results, obviously, we could regulate the onset poten-



**Figure 2** FTIR spectrum of the undoped PTh film obtained at a current density of 1 mA/cm<sup>2</sup>.



**Figure 3** Linear-sweep voltammograms of thiophene electropolymerization on a platinum disc (diameter-0.2 cm) in 12 mmol  $\text{L}^{-1}$  thiophene and a  $\text{CH}_3\text{CN}$  solution with BFEE proportions of (—)4% and (...) 90%, and 0.5 mol/ $\text{L}^{-1}$  thiophene and a 0.1 mol  $\text{L}^{-1}$   $\text{Bu}_4\text{NPF}_6 + \text{CH}_3\text{CN}$  solution without BFEE (insert). Scan rate-50 mV/s<sup>-1</sup>.

tial of the thiophene electropolymerization between 1.16 and 1.75 V by varying the concentration of BFEE, which would be very useful in the electrochemical copolymerization of thiophene with other aromatic monomers.

As shown in Table I, the polymerization rate increased with increasing ratio of BFEE in the mixed solution up to 40%, and then, it decreased. According to the normally accepted mechanism, the polymerization of thiophene was initiated by the electrochemical generation of a radical cation of the monomer. After this step, two radicals are coupled to a dimer, and then, two protons are eliminated. This is a reversible chemical procedure,<sup>22</sup> and a high proton concentration in the electrolyte would suppress the reaction rate.<sup>23</sup> However, this reaction is also favored by the rapid generation of radical cations.<sup>24</sup> At a given applied potential ( $E$ ), the polymerization rate is exponential to the potential difference between  $E$  and the oxidation potential of the monomer ( $E^0$ ).<sup>25</sup> Thus, the total polymerization rate is controlled by the two factors described previously. So, the increase in the polymerization rate with the ratio of BFEE from 4 to 40% benefited from the decrease in the oxidation potential of the monomer (i.e., the increase of  $E - E^0$ ), and the decrease with even higher BFEE concentrations was probably due to a lower ionic conductivity of the electrolyte solution.

The presence of BFEE in the acetonitrile solution also improved the uniformity of the polymer films deposited on the electrode. The surface morphology of the obtained films was investigated by scanning electron microscopy (SEM). Figure 4 shows the SEM photographs of the as-prepared PTh film (in its oxidized state). The film obtained in the solution without BFEE

**TABLE I**  
Effect of BFEE Concentration on the Electropolymerization Potentials of Thiophene and the Conductivity of the As-Prepared PTh Films

$C_{\text{BFEE}}$	$E$ (V)	$I$ (mA)	$(E - E^0)$ (V) <sup>a</sup>	$\sigma_{\text{solution}}$ (mS cm <sup>-1</sup> )	$\sigma_{\text{polymers}}$ (S cm <sup>-1</sup> )
Bu <sub>4</sub> NPF <sub>6</sub> <sup>b</sup>	1.75	0.723	—	24.4	16.9
4%	1.52	0.581	0.28	16.7	34.7
20%	1.47	0.630	0.33	14.2	68.4
40%	1.42	0.682	0.38	13.1	85.1
80%	1.35	0.633	0.45	8.61	116.7
90%	1.23	0.353	0.57	4.91	129.3
95%	1.16	0.342	0.64	3.54	42.2
100%	0.99	0.336	—	2.65	21.7

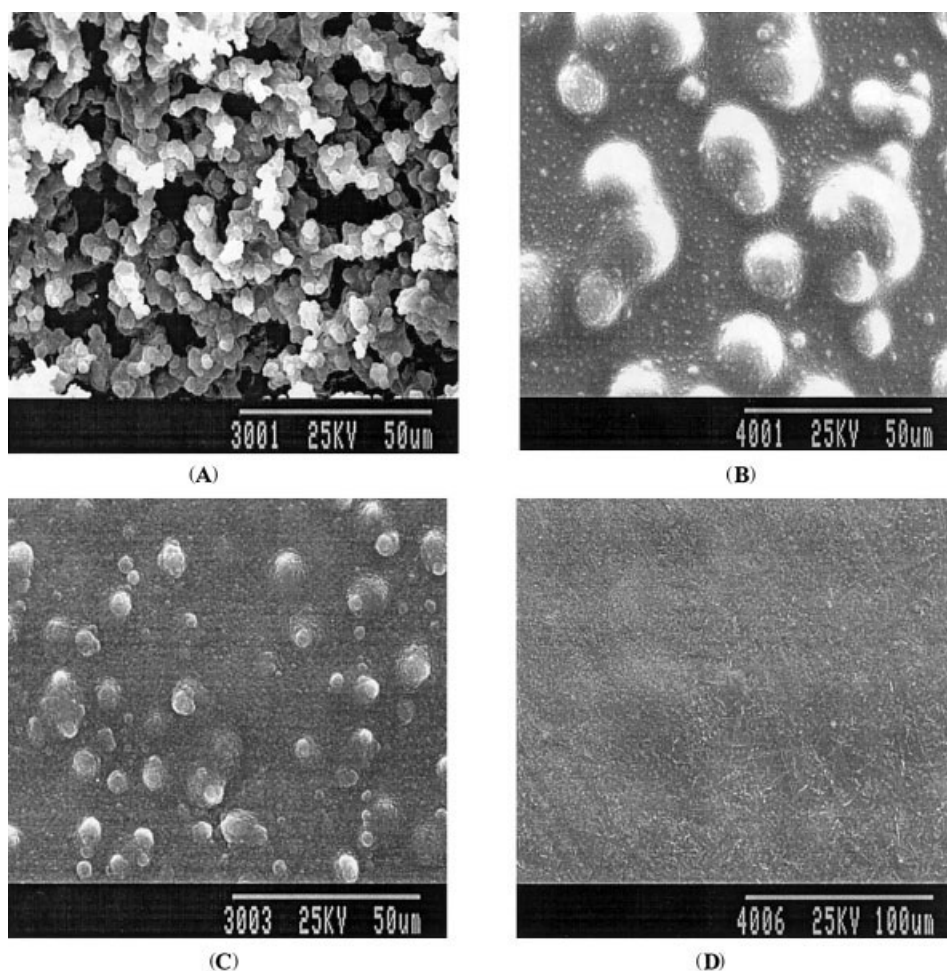
$C_{\text{BFEE}}$  = Volume proportion of BFEE in the acetonitrile solution with 12 mmol L<sup>-1</sup> thiophene  $E$  = Onset potential of the polymerization;  $I$  = Current at 1.8 V on the platinum disc (diameter = 0.2 cm).

<sup>a</sup>The  $E = 1.8$  V.

<sup>b</sup> 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution containing 0.5 mol L<sup>-1</sup> thiophene without BFEE.

showed a porous morphology. With increasing BFEE proportion in the acetonitrile solution, the film surfaces became more and more compact and smooth. The existence of BF<sub>3</sub>OEt<sup>-</sup> anion may have improved the uniformity of the PTh film.

The effect of BFEE concentration on the conductivity of the as-prepared PTh films is also shown in Table I. The conductivity values of the as-prepared films in the acetonitrile solutions with BFEE were much better than those of the films obtained in acetonitrile solution



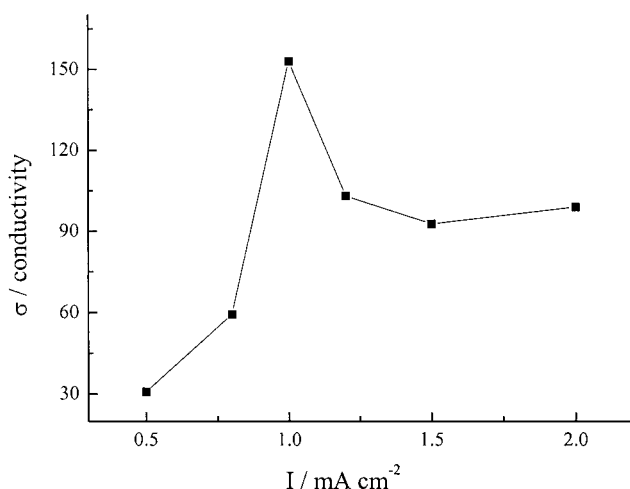
**Figure 4** SEM photographs of the PTh films (solution side) prepared at current density of 1 mA/cm<sup>2</sup>, for 30 min in the acetonitrile solutions with (A) Bu<sub>4</sub>NPF<sub>6</sub> + 0.5 mol L<sup>-1</sup> thiophene, (B) 2% BFEE, (C) 20% BFEE, and (D) 80% BFEE. The thiophene concentration was 12 mmol L<sup>-1</sup> for (B)–(D).

with  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte or in pure BFEE. The values increased with increasing BFEE concentration for those films prepared in the acetonitrile with BFEE as the supporting electrolyte. The increase in conductivity might have resulted from the longer conjugation length and more uniform films of the as-prepared PTh. The former would have facilitated intrachain electron transfer, whereas the latter would have assisted the interchain electron-transfer process.<sup>26</sup> Obviously, the lower polymerization potential in acetonitrile with BFEE was beneficial to the preparation of PTh films with higher conductivities. It is interesting that the conductivities of the films obtained in the acetonitrile solutions with BFEE as electrolyte were higher than that of the film obtained from pure BFEE solution. The origin of this effect is under investigation.

Tanaka et al. investigated the effect of monomer concentration on the thiophene electropolymerization in the electrolyte solutions with various organic solvents.<sup>11</sup> They found that PTh film could not be produced if the thiophene concentration was lower than a minimal value ( $0.1 \text{ mol L}^{-1}$  in the acetonitrile solution). Moreover, the obtained film was brittle if the concentration of thiophene monomer is low. The results reported here suggest that it is possible to obtain a flexible, shiny, and high-conductivity PTh film even in a millimolar concentration of thiophene in binary solutions.

#### Effects of polymerization current and monomer concentration

Table I shows that the PTh film with the highest conductivity was prepared from the binary solvent solution consisting of acetonitrile (10%) and BFEE (90%). Hence, this binary solvent system was used to



**Figure 5** Conductivity of BFEE-doped PTh films deposited on platinum versus current density at a constant monomer concentration (50 mM).

**TABLE II**  
Conductivity and Mechanical Tensile Strength of the PTh Films Prepared in the Solution Containing Acetonitrile (10%) and BFEE (90%) at  $1 \text{ mA/cm}^2$

$10^2 c_{\text{Th}}$ ( $\text{mol L}^{-1}$ )	Conductivity ( $\text{S cm}^{-1}$ )	Mechanical tensile strength (MPa)
1.2	129	47
2.5	121	31
5.0	153	60
8.0	111	52
10	108	51

study the effects of monomer concentration and polymerization current on the electropolymerization processes. Figure 5 shows the effect of polymerization current on the conductivity of the PTh films in 50 mM thiophene with a 10% acetonitrile and 90% BFEE solution. The maximum conductivity of the PTh films, 153 S/cm, was obtained at a current density of  $1 \text{ mA/cm}^2$ . To study the effect of thiophene monomer concentration, we carried out the electropolymerization at a constant current density of  $1 \text{ mA/cm}^2$  in the 10% acetonitrile and 90% BFEE solution with various monomer concentrations. The conductivity and mechanical properties of the PTh films as prepared are listed in Table II. The results indicate that the optimal monomer concentration was 50 mM for the electropolymerization at  $1 \text{ mA/cm}^2$  in the binary solution.

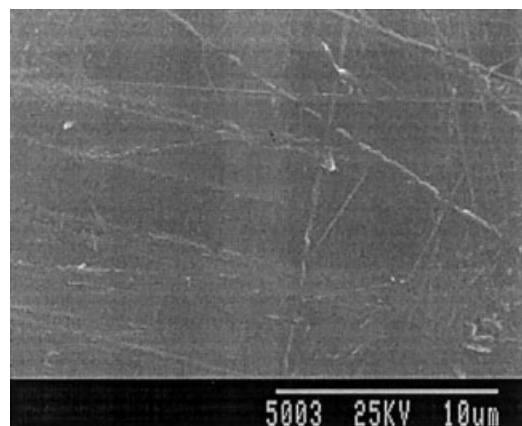
These results indicate that the conductivity and mechanical properties of the PTh films depended on the polymerization conditions, including current density and monomer concentration. Actually, the dependence of the PTh properties on the preparation conditions has been widely studied in literature.<sup>23,27,28</sup> At a constant monomer concentration, if the current density is too high or too low, the conductivity decreases. This phenomenon has been ascribed to the arrangement of the PTh chain and a possible side reaction. The conductivity was determined by both the intrachain charge carrier (polar or bipolar) transportation and the interchain charge carrier transportation. The more ordered arrangement of the chain favors the easier interchain charge carrier transportation. If the current density is too high, the deposition rate of the PTh will be too fast to arrange the chain, and the interchain charge carrier transportation will be more difficult. A lower current usually produces better stereoregularity of the PTh films. However, if the current density is too low, such as lower than  $1 \text{ mA/cm}^2$  in this work, a longer polymerization time is needed, side reactions may compete with the electrochemical reaction, and relatively more oligomers may be produced at a lower current density. When more oligomer is incorporated into the film, the space between the polymer chain is larger, and the interaction of the chain is more difficult. Hence, the conductivity and

mechanical properties will decrease. So, at a lower or higher current density, less quality PTh films are prepared. For the monomer concentration effect, there exist two competitive reactions on the electrode at the potentials for thiophene electropolymerization: one is the oxidative electropolymerization of thiophene, and the other is the overoxidation of the PTh film. If the monomer concentration is too low to supply enough thiophene molecules on the electrode for the electropolymerization, overoxidation degradation of the PTh film formed on the electrode will occur, which will decrease the conductivity and mechanical properties of the film. Hence, higher monomer concentrations can prevent the overoxidation and produce the PTh films. However, if the monomer concentration is higher than a proper value, such as 50 mM in the binary solvent solution, some thiophene oligomers may be deposited into the PTh films on the electrode, which will result in a decrease in the conductivity and mechanical properties of the films. Obviously, a current density of 1 mA/cm<sup>2</sup> and a monomer concentration of 50 mM were the optimal electropolymerization conditions for thiophene in the binary solvent solution.

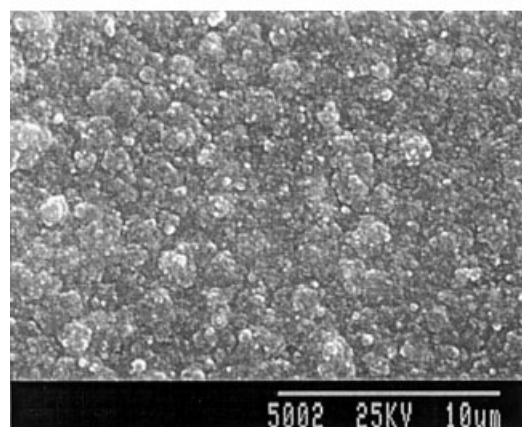
#### Morphology, conductivity and mechanical properties

Figure 6 presents the SEM images of the two sides of the PTh film prepared on platinum sheet under the optimal electropolymerization conditions. The morphologies of the two sides of the PTh film were different. The side in contact with the electrode was flat and compact, and the side in contact with the solution was relatively rougher. This result, in accordance with the theory, implied that the density of the polymer layer decreased with the film thickness, that is, from the metal surface to the polymer/solution interface.<sup>29</sup> The polymerization process could be distinguished by two or more stages. The first compact layer was formed on the electrode surface via two-dimensional growth, whereas in the advanced stage, one-dimensional growth of the polymer chain with continuous branching led to an open structure. After the first compact layer was formed, three-dimensional growth occurred.

The conductivity of the PTh film prepared at the optimal conditions was 153 S cm<sup>-1</sup>, which was about four times higher than the value of 40 S cm<sup>-1</sup> for the PTh film prepared in pure BFEE. The mechanical tensile strength of the film measured at room temperature was about 60 MPa at a stretching rate of 0.5 cm/min<sup>-1</sup>, and its elongation at break was about 10 ± 1%. This mechanical tensile strength value was much higher than those of some widely used engineering plastics, such as polypropylene (26 MPa) and poly(vinyl acetate) (30 MPa).



(a)



(b)

**Figure 6** SEM micrographs of the PTh film deposited on the platinum electrode from the binary solvent solution consisting of acetonitrile (10%) and BFEE (90%): (a) the side in contact with the electrode in the doped state and (b) the side in contact with the solution in the doped state.

#### CONCLUSIONS

BFEE was first used as the supporting electrolyte in the electrochemical polymerization of thiophene in acetonitrile solution. The onset potential of the oxidative polymerization of thiophene decreased with increasing BFEE concentration, and it was regulated between 1.75 and 0.99 V by changes in the BFEE concentration. The PTh films prepared in the acetonitrile solutions with BFEE were flexible and compact. The conductivity of the films increased with increasing BFEE concentration in the acetonitrile solutions until the BFEE proportion reached 90 vol %. In addition, high-quality PTh films were obtained under the optimal polymerization conditions, with a monomer concentration of 50 mM and a current density of 1 mA/cm<sup>2</sup> in a binary solvent solution consisting of 10% acetonitrile and 90% BFEE.

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