

# Poly(3-Chlorothiophene) Films Prepared by the Direct Electrochemical Oxidation of 3-Chlorothiophene in Mixed Electrolytes of Boron Trifluoride Diethyl Etherate and Sulfuric Acid

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**ABSTRACT:** 3-Chlorothiophene (CT) was electrochemically polymerized in mixed electrolytes of a boron trifluoride diethyl etherate solution containing 0–20% (by volume) sulfuric acid. The oxidation potentials of the monomer in these media were measured to be only 1.06–1.31 V (vs Ag/AgCl). These values were much lower than that of CT in

acetonitrile and 0.1 mol/L (Bu)<sub>4</sub>NBF<sub>4</sub> (1.92 V vs Ag/AgCl). Poly(3-chlorothiophene) (PCT) films with conductivities of 0.1–2 S cm<sup>-1</sup> were obtained. The structure, morphology, and electrochemical behavior of the PCT films also were investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 502–509, 2003

## INTRODUCTION

Polythiophene and its derivatives have attracted considerable attention over the past 20 years,<sup>1–6</sup> mainly because of their remarkable solid-state properties, including their stability in the atmosphere, high conductivity, and ease in forming free-standing and high-strength films. There are tremendous technological potentials for polythiophenes in electrocatalysis<sup>7</sup> and in the fabrication of molecular electronic devices,<sup>8</sup> solid-state batteries,<sup>9</sup> chemically modified electrodes,<sup>10</sup> and biosensors.<sup>11,12</sup> Polythiophene and a number of its derivatives have been synthesized and studied extensively. However, only a few articles have reported poly(3-halide thiophene)s,<sup>13–17</sup> and among them, only one short communication is concerned with the direct oxidation of 3-chlorothiophene (CT).<sup>14</sup> The oxidation of CT requires a very high potential in a neutral solvent (2.18 V vs saturated calomel electrode), and the polymer obtained from this medium is powdery and has low conductivity (<10<sup>-2</sup> S cm<sup>-1</sup>).<sup>14</sup>

However, free-standing polythiophene<sup>18–20</sup> and poly(*para*-phenylene) films<sup>21–23</sup> with high strengths and fairly good flexibility can be prepared by the direct anodic oxidation of corresponding monomers in

pure boron trifluoride diethyl etherate (BFEE). Furthermore, the oxidation potentials of the monomers can be lowered greatly. The addition of a superacid, such as trifluoroacetic acid or sulfuric acid (SA), to BFEE can further decrease the oxidation potential of benzene and improve the quality of the polymer film.<sup>22,23</sup> However, mixed electrolytes of BFEE and superacid have never been used for the electrochemical polymerization of thiophene and its derivatives.

On this basis, we report here the electrochemical polymerization of CT in mixed electrolytes of BFEE and SA. The oxidation potential of the monomer was found to be very low (1.06–1.31 V vs Ag/AgCl) in these media, and poly(3-chlorothiophene) (PCT) films with conductivities of 0.1–2 S cm<sup>-1</sup> were obtained.

## EXPERIMENTAL

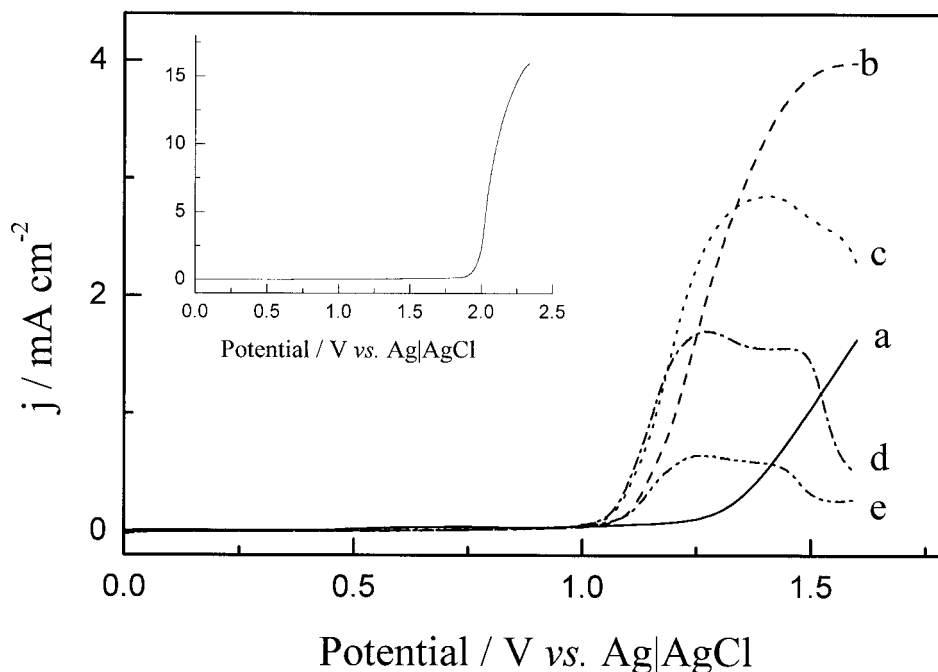
### Chemicals

3-chlorothiophene (CT) (98%) was purchased from Acros Organics, Fisher Scientific World Wide Co. (Geel, Belgium). BFEE was a fresh product of Beijing Changyang Chemical Plant (Beijing, China) and had a BF<sub>3</sub> concentration of 48.24% (by volume). SA (98%) was bought from Beijing Lishui Chemical Plant (Beijing, China), and 25% ammonia was obtained from Beijing Yili Chemical Products Co., Ltd. (Beijing, China). Commercial high performance liquid chromatography (HPLC)-grade acetonitrile was manufactured by Tianjin Siyou Bio-Medical and Technology Co (Tianjin, China). All these materials were used as received. Tetrabutylam-

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**Figure 1** Anodic polarization curves of CT in electrolytes of BFEE mixed with (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20% SA (by volume) or in acetonitrile and 0.1 mol/L TBATFB (insert). The potential scan rate was  $20 \text{ mV s}^{-1}$ .

monium tetrafluoroborate [TBATFB;  $(\text{Bu})_4\text{NBF}_4$ ; 98%; Fluka Buchs SGL, Switzerland) was dried in vacuo at  $60^\circ\text{C}$  for 24 h before use.

### Instruments and procedures

The electrochemical polymerizations and examinations were performed in a one-compartment cell with a model 283 potentiostat/galvanostat (EG&G Princeton Applied Research, Oak Ridge, TN) under computer control. For the electrochemical examinations, Pt wires (1 mm in diameter) were used as the working and counter electrodes. For film growth, the working and counter electrodes were two stainless steel sheets (AISI 304,  $1.8 \text{ cm} \times 6 \text{ cm}$ ) placed 0.5 cm apart. Before each polymerization, they were carefully polished with abrasive paper (1200-mesh); were cleaned with water, methanol, and acetone successively; and were finally dried with a blower. All potentials were referred to a wire electrode (Ag/AgCl) immersed directly in the solution.

The typical electrolytic solutions were mixtures of BFEE and SA (0–20 vol %). All solutions were deaerated with a dry nitrogen stream for 5–10 min, and a slight nitrogen overpressure was maintained during the experiments.

PCT films were prepared potentiostatically. Their thickness was controlled by the total charges passed through the cell, and the charge values were read directly from  $i$ - $E$  curves by a computer. After polymerization, PCT films were peeled off or scraped from

the electrode surfaces and then washed repeatedly with distilled diethyl ether for the removal of the electrolyte and monomer. For electrochemical studies, Pt electrodes coated with the polymer were also rinsed with diethyl ether and dried with a blower.

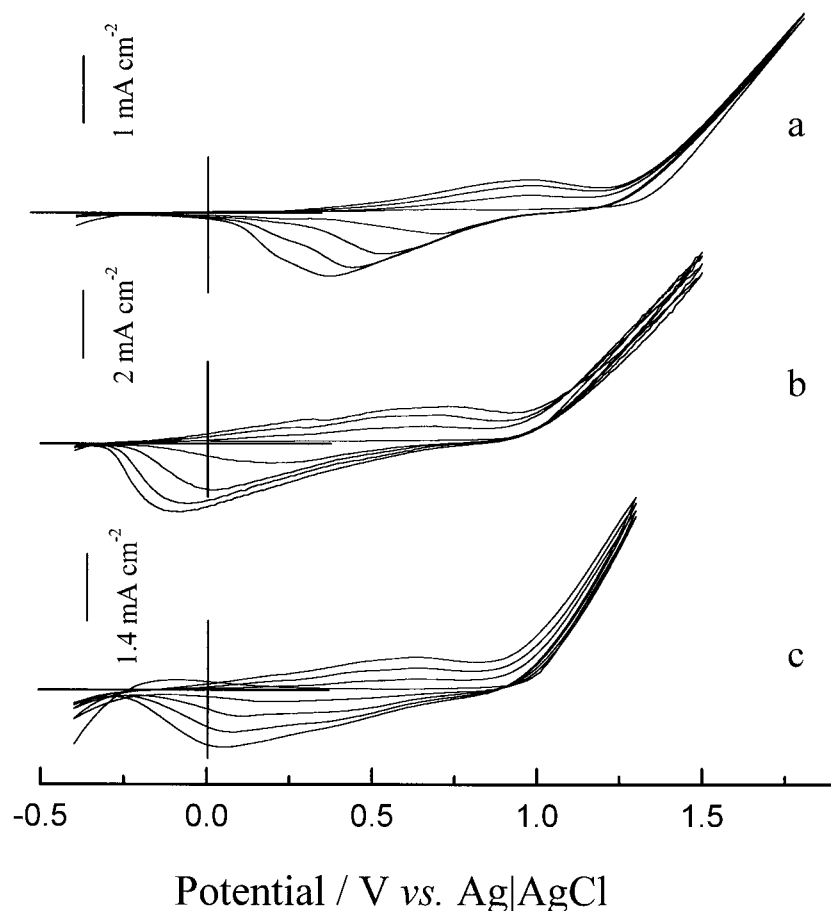
For infrared (IR) spectral studies, polymer films were dedoped with 25% ammonia for 3 days and then washed repeatedly with distilled water and acetone. Finally, they were dried in vacuo at  $60^\circ\text{C}$  for 12 h. The IR spectra were taken with KBr pellets of the polymers on an Avatar 360 Fourier transform infrared (FTIR) spectrometer (Nicolet Instrument Corporation, Madison, WI). Raman spectra were created with an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 633-nm laser beam and a charge coupled device (CCD) detector with a  $4\text{-cm}^{-1}$  resolution. The spectra were recorded with a  $50\times$  objective, and the laser power was always kept very low ( $\sim 0.1 \text{ mW}$ ) to avoid the destruction of the samples.

Scanning electron micrographs were taken with a KY 2800 electron micrographer (Scientific Instrumental Plant, Chinese Academy of Sciences, Beijing, China). The conductivities were measured with the conventional four-probe technique.

## RESULTS AND DISCUSSION

### Electrochemical polymerization of CT

Figure 1 shows the anodic polarization curves of CT in the solvents of BFEE mixed with 0–20% SA (by vol-



**Figure 2** Successive CVs of 0.1 mol/L CT in (a) BFEE, (b) BFEE and 5% SA, and (c) BFEE and 10% SA. The potential scan rate was  $100 \text{ mV s}^{-1}$ .

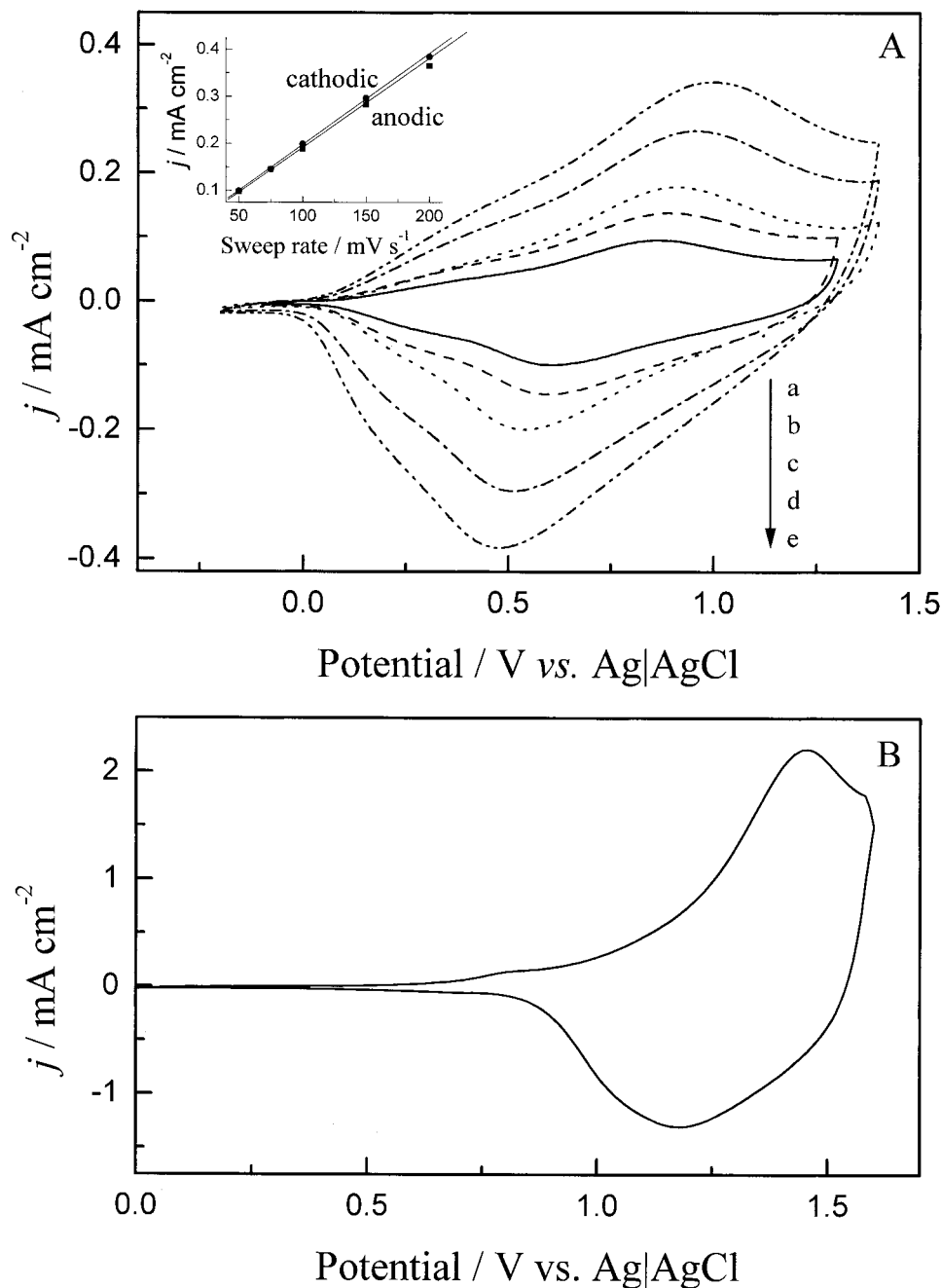
ume). The virgin oxidation of CT in pure BFEE was initiated at 1.31 V versus Ag/AgCl. This value was much lower than that of CT in acetonitrile containing 0.1 mol/L TBATFB (1.92 V vs Ag/AgCl), as shown in the insert of Figure 1. The addition of 5% SA (by volume) to BFEE decreased the oxidation potential of the monomer to 1.08 V, and the polymerization rate was also accelerated. This was mainly because SA increased the ionic conductivity of the electrolyte. The lowest oxidation potential of the monomer was detected in the medium of BFEE containing 10% SA. However, a further increase in the SA content in the mixed electrolytes suppressed the polymerization rate and increased the oxidation potential of the monomer [Fig. 1(d,e)]. According to the normally accepted mechanism, the polymerization of thiophenes is initiated by the electrochemical generation of the radical cations 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>24</sup> and a high proton concentration in the electrolyte would decrease the dimerization (or polymerization) rate.<sup>25</sup> This explains the results shown in Figure 1(c–e).

Successive cyclic voltammograms (CVs) of 0.1 mol/L CT in mixed electrolytes on Pt electrodes are

illustrated in Figure 2. During the first CV cycles, the currents on the reverse scans are much higher than those on the forward scans in the regions of 1.2–1.7 [Fig. 2(a)], 1.0–1.5 [Fig. 2(b)], and 0.9–1.1 V [Fig. 2(c)]. The formation of these loops is characteristic of a nucleation process, which has been reported in the literature.<sup>26,27</sup> In pure BFEE [Fig. 2(a)], the polymer was reduced and oxidized between 0.0 and 1.2 V. The increase in the redox wave currents implied that the amount of the polymer on the electrode was increasing. The potential shift of this wave current maximum provides information about the increase in the electrical resistance in the polymer film and the overpotential needed to overcome the resistance.<sup>28</sup> The overall features of Figure 2(b,c) are similar to those of [Fig. 2(a)], indicating similar electrochemical behaviors.

#### Electrochemistry of PCT films

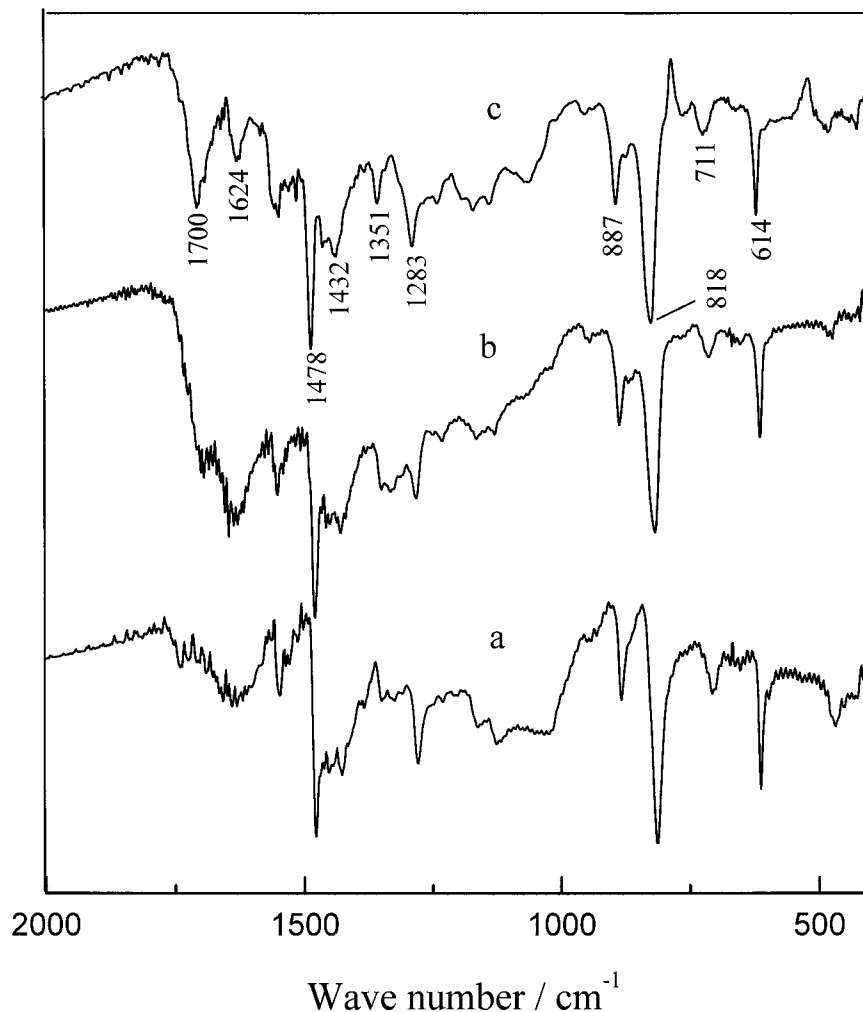
The electrochemical behavior of PCT films electrochemically deposited from pure BFEE was studied in pure BFEE [Fig. 3(A)] and in acetonitrile and 0.1 mol/L TBATFB for comparison [Fig. 3(B)]. Similar to the results in the literature,<sup>10</sup> the steady-state cyclic



**Figure 3** CVs of PCT films (A) in pure BFEE at potential scan rates of (a) 50, (b) 75, (c) 100, (d) 150, and (e) 200  $\text{mV s}^{-1}$  or (B) in acetonitrile and 0.1 mol/L TBATFB at a potential scan rate of 100  $\text{mV s}^{-1}$ . The PCT films were electrochemically synthesized in pure BFEE and 0.1 mol/L CT at a constant applied potential of 1.5 V versus Ag/AgCl. The film thickness was 250 nm.

CVs represented broad anodic and cathodic peaks. The current densities were proportional to the scan rate [Fig. 3(A), insert], indicating a redox couple fixing on the electrode.<sup>2</sup> Furthermore, these films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials. In BFEE, the PCT film could be oxidized and reduced from 0.99 to  $-0.48$  V, whereas in acetonitrile, much higher potentials were

needed to oxidize or reduce the film [from 1.45 to 1.17 V; Fig. 3(B)]. Substituted polythiophenes prepared from nonsymmetric monomers usually show broad redox waves in their CVs.<sup>5</sup> This phenomenon is ascribable to the presence of coupling defects distributed statically, which result in a series of energetically non-equivalent chain segments. PCT films obtained from mixed electrolytes showed an electrochemical behavior similar to that displayed in Figure 2.



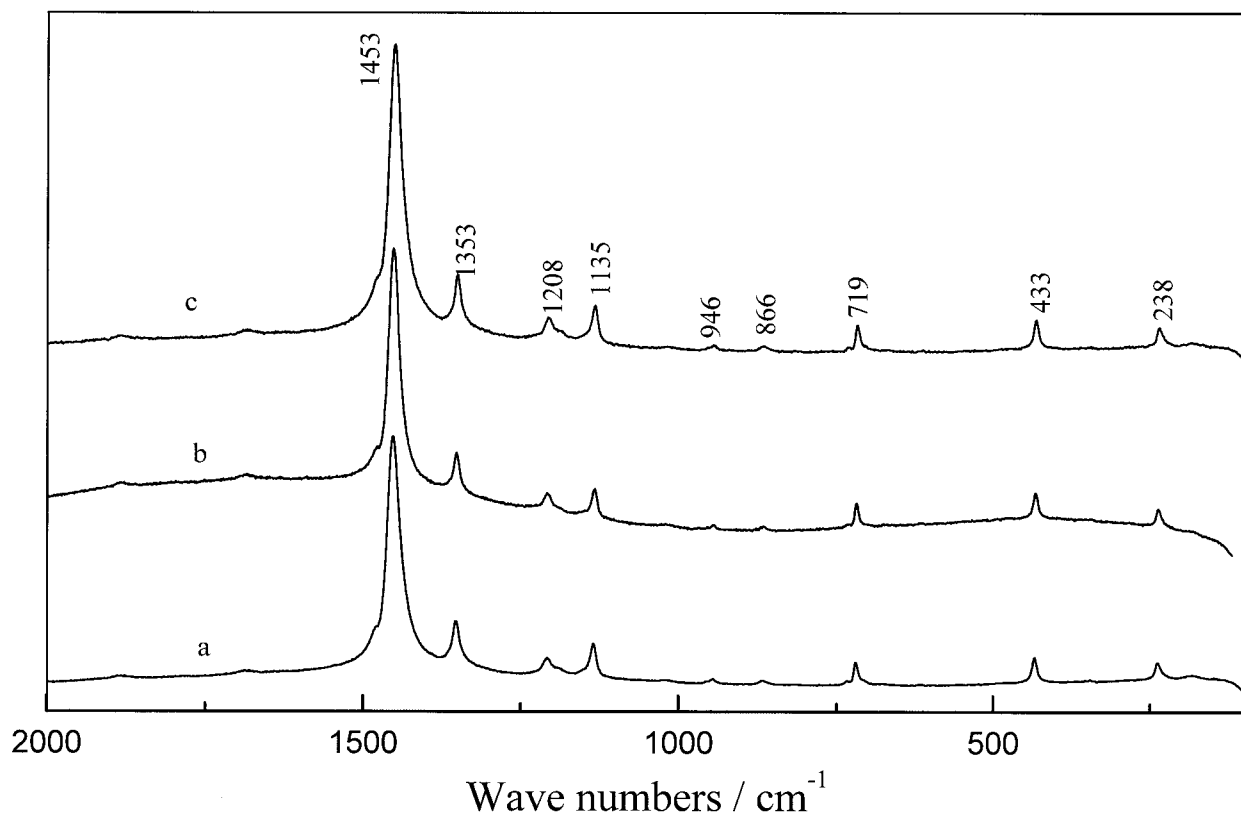
**Figure 4** FTIR spectra of PCT films obtained potentiostatically at 1.5, 1.3, and 1.3 V versus Ag/AgCl from 0.1 mol/L CT with electrolytes of BFEE containing (a) 0, (b) 5, and (c) 10% SA, respectively.

To study the electrochemical stability of PCT films, we also performed CV studies in concentrated SA over the potential range of 0.1–1.3 V versus Ag/AgCl. As in BFEE and acetonitrile, the CVs of PCT films could be cycled repeatedly between conducting and nonconducting states in the full potential range with no significant decomposition of the materials, and wave currents also scaled linearly with the potential scan rate. The half-wave potential ( $E_{1/2}$ ) of PCT films was determined to be approximately 0.60 V. These results indicated that the PCT films were electrochemically stable in concentrated SA for the potential scale of 0.1–1.3 V.

#### Spectra of PCT films

The transmittance FTIR spectra of PCT films obtained from pure BFEE, mixed electrolytes of BFEE and 5% SA, and mixed electrolytes of BFEE and 10% SA are presented in Figure 4. The band at approximately 1478

$\text{cm}^{-1}$  was attributed to the antisymmetric C=C stretching vibration of the thiophene ring. The bands centered at approximately 1432  $\text{cm}^{-1}$  were assigned to the symmetric stretching vibration of the thiophene ring C=C. The 1283- $\text{cm}^{-1}$  band was due to the C—C deformation, and the antisymmetric stretching vibration of the C—C bond showed absorption at approximately 1351  $\text{cm}^{-1}$ .<sup>29,30</sup> The characteristic IR bands of PCT were located around 600–900  $\text{cm}^{-1}$ , and the bands centered at approximately 887  $\text{cm}^{-1}$  were assigned to the antisymmetric and symmetric C—S stretching vibrations. The very strong absorption at approximately 818  $\text{cm}^{-1}$  was associated with the C—H out-of-plane deformation of the 2,5-disubstituted thiophene ring (due to  $\alpha$ - $\alpha'$  coupling) and the band at approximately 711  $\text{cm}^{-1}$  was ascribed to the C—H out-of-plane vibration of the monosubstituted thiophene ring.<sup>30–32</sup> The stretching vibration of C—Cl was located at 614  $\text{cm}^{-1}$ . According to the literatures,<sup>30–32</sup> the average degree of polymerization (DP)



**Figure 5** Raman spectra of PCT films obtained potentiostatically from 0.1 mol/L CT with electrolytes of (a) pure BFEE, (b) BFEE and 5% SA, and (c) BFEE and 10% SA. The film thickness was 4  $\mu\text{m}$ .

of polythiophene films can be evaluated from the integrated intensity ratios of the bands at 818 and 711  $\text{cm}^{-1}$ . Therefore, the DPs of PCTs obtained from pure BFEE and mixed electrolytes were calculated to be 18–21. Furthermore, there is a strong band at approximately 1700  $\text{cm}^{-1}$  in Figure 4(c), most probably due to overoxidation of the polymer.

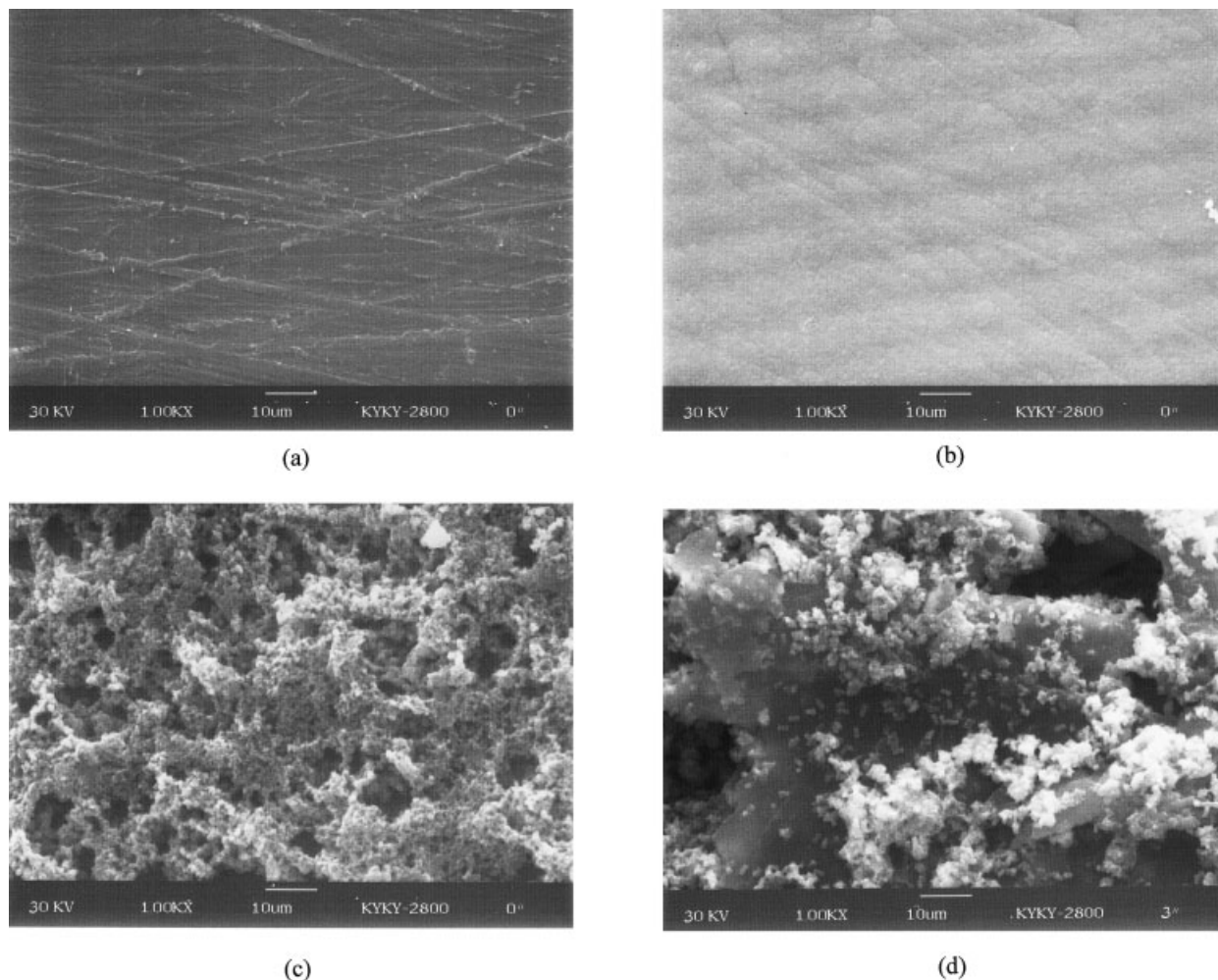
The Raman spectra of PCT films prepared from pure BFEE, BFEE and 5% SA, and BFEE and 10% SA are shown in Figure 5. A weak fluorescence background and a high signal-to-noise ratio are found in these spectra. Despite their complex chemical structures, the Raman spectra of these polymers are rather simple.<sup>33</sup> The band around 1400–1500  $\text{cm}^{-1}$  is a common feature of Raman spectra of aromatic and heteroaromatic systems; it is always strong and dominates the entire Raman spectrum.<sup>33–41</sup> As can be seen in Figure 5(a), the most intense band was located at approximately 1453  $\text{cm}^{-1}$  and was assigned to the totally symmetric in-phase  $\nu(\text{C}=\text{C})$  vibration of the bulk thiophene rings spreading over the whole polymer chain. The band at approximately 1490  $\text{cm}^{-1}$  originated from the antisymmetric stretching modes mostly localized at either end of the polymer chain. The weak bands at approximately 1353 and 1208  $\text{cm}^{-1}$  in the spectra were assigned to the  $\text{C}_\beta\text{—C}_{\beta'}$  and  $\text{C}_\alpha\text{—C}_{\alpha'}$  ring stretching, respectively. The well-de-

fined and characteristically sharp and medium-strong scattering near 1135  $\text{cm}^{-1}$  was associated with the totally symmetric in-plane wag of the C—H groups in the position of  $\beta'$ . The very weak bands at approximately 946 and 866  $\text{cm}^{-1}$  originated from the stretching of the thiophene ring. The bands of C—S—C deformation appeared at 734 and 719  $\text{cm}^{-1}$ . The bands at approximately 433 and 238  $\text{cm}^{-1}$  were assigned to C—Cl deformation.

### Morphology and conductivities of PCT films

Figure 6 presents typical scanning electron micrographs of PCT films prepared from electrolytes of pure BFEE, BFEE and 5% SA, and BFEE and 10% SA. A free-standing PCT film was obtained from pure BFEE, and the two sides of the film were flat and compact. However, the polymer films deposited from the mixed electrolytes were powdery. The film surface in contact with the solution was rough and irregular [Fig. 6(c,d)].

The conductivity of the PCT film obtained from pure BFEE was measured to be only 0.1  $\text{S cm}^{-1}$ . Adding SA to the electrolyte improved the conductivity of the PCT film. The conductivity of the PCT film prepared from BFEE and 5% SA was determined to be 2  $\text{S cm}^{-1}$ . However, the PCT film synthesized in BFEE



**Figure 6** Scanning electron micrographs of PCT films obtained potentiostatically from 0.1 mol/L CT with electrolytes of (a,b) pure BFEE, (c) BFEE and 5% SA, and (d) BFEE and 10% SA: (a) the side in contact with the electrode and (b–d) the sides in contact with the solution.

and 10% SA showed a relatively low conductivity of  $0.6 \text{ S cm}^{-1}$  that was probably due to overoxidation of the polymer, as described previously.

### CONCLUSIONS

CT was electrochemically polymerized in a BFEE solution, and its oxidation potential was determined to be 1.31 V, which was much lower than that in acetonitrile, 1.92 V versus Ag/AgCl. At an applied potential of 1.5 V versus Ag/AgCl, a free-standing, flat PCT film was obtained. When a small amount of concentrated SA was added ( $\leq 10\%$  by volume), the oxidation potentials of the monomer were lowered further to approximately 1.06 V, and the polymerization rate was also accelerated. The as-formed PCT films showed good redox properties and high stability in BFEE, acetonitrile, and concentrated SA. The conductivity of the polymer film was improved but its mechanical properties were reduced by SA addition.

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