

Electrosynthesis of Free-Standing Poly(*para*-phenylene) Films in Mixed Electrolytes of Boron Trifluoride Diethyl Etherate and Trifluoroacetic Acid on Stainless Steel Electrode

CHUN LI,¹ FENG CHEN,² GAOQUAN SHI,² JINGKUN XU,² ZHENGJIANG XU²

¹ Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

² Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

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ABSTRACT: Free-standing poly(*para*-phenylene) (PPP) films have been electrosynthesized by direct oxidation of benzene on stainless steel electrode in mixed electrolytes of boron trifluoride diethyl etherate (BFEE) and trifluoroacetic acid (TFA). The oxidation potential of the monomer in these media is lower than those in the neutral media. Increasing the content of TFA in the mixed electrolyte can effectively decrease the oxidation potential and increase the coupling rate of the monomer. The films obtained from these media were very shiny and flexible, and could easily be processed into various shapes by conventional mechanical methods. The films had a linear chain structure, and their degree of polymerization could be improved by increasing the TFA content in the mixed electrolyte. Moreover, the films had a fairly good thermal stability. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2462–2466, 2002

Key words: poly(*para*-phenylene); electrosynthesis; free-standing film; mixed electrolyte; stainless steel electrode

INTRODUCTION

Conducting polymers have long delocalized conjugation structures, and most of them are brittle and have low mechanical strengths. Furthermore, these materials are insoluble, intractable, or decompose before melting.^{1–3} They cannot be shaped by conventional polymer-processing techniques. Therefore, the synthesis of high-strength and flexible conjugated polymers is an exciting challenge from the point of view of both synthesis

itself and potential applications based on these materials.^{3,4} Up to now, most effects regarding electrochemical polymerization have been concerned with heteroaromatic compounds such as pyrrole, thiophene, and their derivatives as well as aniline and derivatives. Although the number of publications devoted to the electrochemical synthesis of poly(*para*-phenylene) (PPP) is considerably small, and probably this fact is related in part to the complicated conditions required as reported by Lacaze and coworkers.⁵ The Lacaze's group has studied on the electrochemical synthesis of PPP in single or mixed acids media, and the results demonstrated that the oxidation potential of benzene was generally lowered in these media. However, the final products obtained from these systems are rather powdery and difficult to be

Correspondence to: G. Shi; e-mail: gshi@tsinghua.edu.cn.
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peeled off from the electrodes.⁶ Despite PPPs having extremely promising properties, the very rigid rod-like structure renders the processing of this material very difficult, and thus the potential technological application of these PPP materials was restricted.³ Recently we found PPP films could be deposited onto a stainless steel electrode in a mixed electrolyte consisting of boron trifluoride diethyl etherate (BFEE) and trifluoroacetic (TFA). These films weakly adhered to the electrode surface and could be easily peeled off into free-standing states by hand. They have great mechanical strengths and flexibility and can be easily processed by conventional mechanical methods into a variety of structures such as fibers, circles, and triangles. Here we report our experimental results.

EXPERIMENTAL

Reagents

Benzene (Shanghai 2nd Chem. Co., China) was twice distilled before use. BFEE (Hangman Chem. Plan, China) and TFA (Merit, 98%) were used as received.

Electrosynthesis and Film Characterization

Electrochemical synthesis was performed in a one-compartment cell with the use of a Model 273 potentiostat (EG&G Princeton Applied Research Co.) under computer control. The working and counter electrodes were AISI 304 stainless steel sheets (2×6 cm) placed 0.5 cm apart. They were carefully polished with abrasive paper (1200 mesh), and cleaned in an ultrasonic acetone bath before each synthesis. All potentials were referred to a saturated calomel electrode (SCE). The typical electrolytic solutions were mixtures of BFEE and TFA containing 1 M benzene with the volume percentages of TFA being 15, 33, and 50% unless otherwise indicated. All solutions were deaerated by a dry argon stream and maintained a slight argon overpressure during the experiments. The integrated charge passed during film growth was used to control the thickness of the deposited films. The PPP films were peeled off the electrode surface and washed repeatedly with distilled diethyl ether and then dried under vacuum at 60°C for 24 h before characterization.

For IR and TGA examination, the PPP films had been dedoped with 25% ammonia for 3 days,

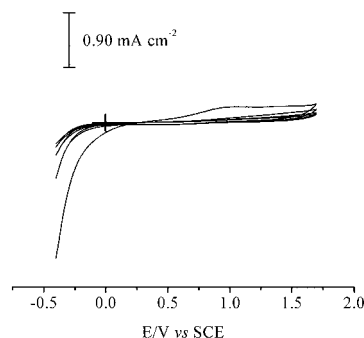


Figure 1 Cyclic voltammograms of stainless steel electrode in the electrolytes of BFEE mixed with 33% (by volume) TFA at a potential scan rate of 100 mV s^{-1} .

and then washed repeatedly with distilled water and acetone. Finally, they were well dried under vacuum at 60°C. The IR spectra were taken out by using KBr pellets of the polymer on a Bruker IFS 66V spectrometer.

Film thickness was determined with a "Heilderham" thickness monitor. Tensile strength of the films was carried out using an electronic drawing machine (WD-1, Changchun) at a stretching rate of 0.5 cm s^{-1} . Scanning electron micrographs were taken out by using an X-560 electron micrographer. Thermogravimetric analysis (TGA) was carried out by using a TGA-DTA V1.1 TA Inst 2100 at a heating rate of $10^\circ\text{C min}^{-1}$ and with sample weight of $3.0 \pm 0.5 \text{ mg}$.

RESULTS AND DISCUSSION

Electrochemical Polymerization

Figure 1 shows typical cyclic voltammogram of stainless steel electrode in monomer free BFEE mixed with 33% (by volume) TFA. As shown in Figure 1, an active-to-passive current peak was clearly observed at ca. 1.0 V on the first anodic scan started from 0.25 V. Note that this peak was nearly not observed again on the successive scans in the same potential region. These results demonstrate that both the stainless steel electrode and the electrolyte were electrochemically inert after the first potential scanning process.

Figure 2 illustrates the anodic polarization curves of benzene in the electrolytes of BFEE mixed with 0–70% (by volume) TFA. The virgin oxidation of benzene is initiated at 1.70, 1.63, 1.60, 1.58, 1.57, 1.55, and 1.55 V (vs. SCE), respectively. The oxidation potential decreases with

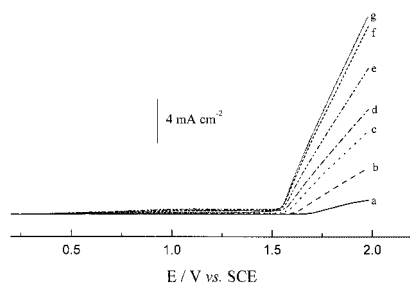


Figure 2 Anodic polarization curves of 1 M benzene in the electrolytes of BFEE mixed with 0% (a), 10% (b), 20% (c), 33% (d), 40% (e), 50% (f), and 60% (g) (by volume) TFA.

the increase of TFA content. All these values are much lower than those observed in neutral media.⁷ At a given applied potential, the current density of the monomer oxidation also increases with TFA content, indicating the increase of polymerization rate.

Figure 3 demonstrates the successive cyclic voltammograms of 1 M benzene in the electrolytes of BFEE mixed with 15 (A), 33 (B), 50% (C) (by volume) TFA in the scanning region of -0.4 – 1.85 V, -0.4 – 1.7 V, and -0.4 – 1.7 V vs. SCE, respectively. As can be seen from this figure, on the first cycle, the cathodic excursion of the potential gives a voltammogram with more anodic current densities in the potential regions of 1.42 – 1.85 V (A), 1.44 – 1.70 V (B), and 1.42 – 1.70 V (C), respectively, than those of the anodic excursion. The formation of these loops is characteristic of the nucleation processes, as reported in the literature,⁸ and only appears on the first voltammogram. At the same time, the potential scans shown led to the formation of the film on the electrode surface. The strong oxidation present at potentials greater than 1.5 V promoted polymer

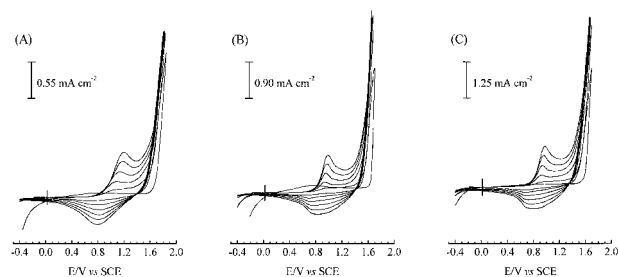


Figure 3 Cyclic voltammograms of 1 M benzene in the electrolytes of BFEE mixed with 15% (A), 33% (B), and 50% (C) (by volume) TFA at a stainless steel electrode and a potential scan rate of 100 mV s^{-1} .

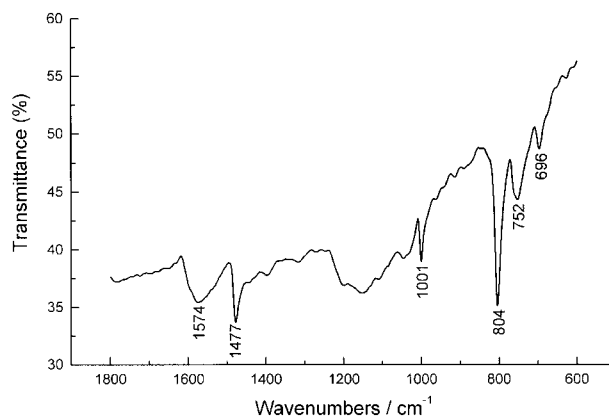


Figure 4 Transmission infrared spectrum of PPP film (KBr pellet) obtained at an applied potential of 1.7 V (vs. SCE) in the electrolyte of BFEE mixed with 33% TFA.

generation on the electrode. The polymer was reduced and oxidized between 0.70 and 1.25 V (A), 0.7 and 1.0 V (B and C), respectively. The increases of the polymer redox wave currents implied that the amount of the polymer on the electrode increased. The potential shift of these maximum provides information about the increase of the electrical resistance in the polymer film and the overpotential needed to overcome that resistance.⁹ It should be noted that the reproducibility of the voltammograms is not very satisfactory. The monomer oxidation potential and the redox current densities of the polymer showed slight dependence on the freshness and the mixing time of the two acids, most probably due to the fact that these acids are highly hygroscopic.

Structure Characterization

The typical transmission infrared spectrum of PPP (KBr Pellet) prepared at 1.7 V in system B is illustrated in Figure 4. The characteristic IR bands of PPP were located around 650 – 900 cm^{-1} . In detail, the band at 804 cm^{-1} is due to the out-of-plane C–H vibration ($\delta_{\text{C-H}}$) of 1,4-disubstituted benzene ring. The $\delta_{\text{C-H}}$ bands of the monosubstituted benzene ring (the terminal benzene ring) appeared at 696 and 752 cm^{-1} .^{10,11} Furthermore, the medium band at 1001 cm^{-1} , is attributed to *para*-substituted C_6H_4 groups,¹² and the band at 1477 cm^{-1} corresponding to C=C aromatic vibration.¹³ This spectrum showed no strong bands at 840 and 860 cm^{-1} , which are ascribed to trisubstituted and tetrasubstituted benzene, respectively, indicating that the princi-

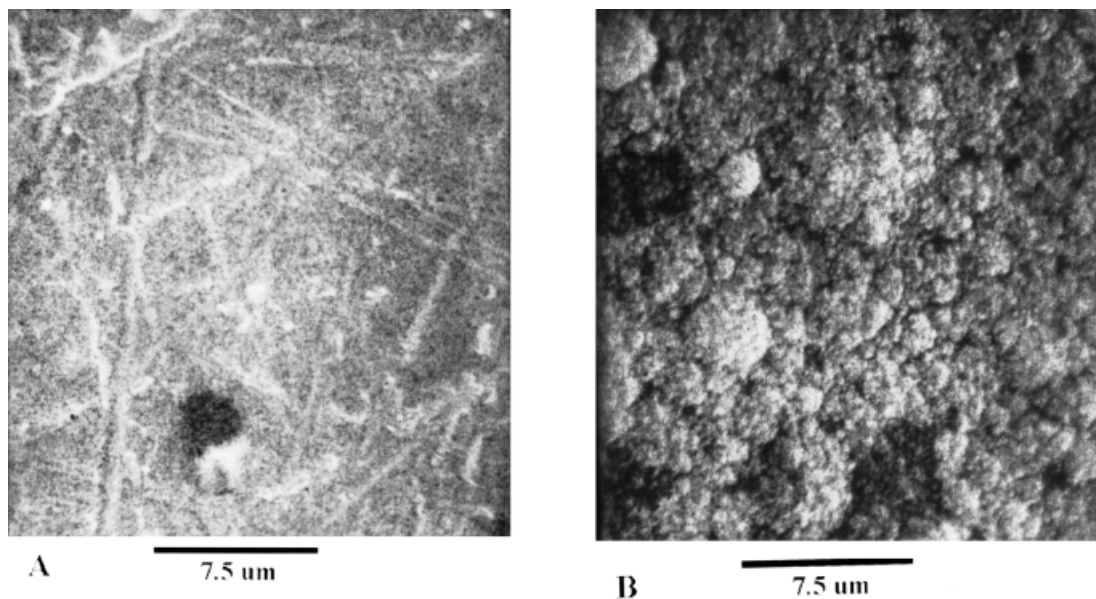


Figure 5 Scanning electron micrographs of the PPP film prepared from the electrolyte of BFEE mixed with 33% TFA; (A) is the side in contact with the electrode, and (B) is the side in contact with the solution. (magnification: 4000 \times).

pal structure of the polymer is linear without crosslinking.^{14,15} However, an additional broad peak appears at 1574 cm^{-1} , which might be result from the presence of crossmoieties in end groups.¹² In conclusion, the PPP films obtained in this media have a high regularity (linear structure) and contain a weak irregularity at the end groups of the backbones. The PPP prepared at other conditions showed similar infrared spectra.

The degree of polymerization (DP) was estimated from the intensities of the bands at 804 and 696 cm^{-1} following the empirical formula $\text{DP} = 2 (I_{804}/I_{696}) + 2$.¹² According to the IR spectra, the PPP obtained by electrochemical polymerization of benzene in the media of BFEE + 15–50% TFA has a number average repeat units of 17–25. The increase of TFA content in the mixed electrolyte can slightly increase the DP of PPP.

Film Properties

The PPP films obtained potentiostatically at 1.7 V (vs. SCE) from the mixed electrolytes were very shiny and flexible, and mechanically behaved like a metal foil. The conductivity of these films, measured by the conventional four probe technique, was ca. $2 \times 10^{-3} \text{ S cm}^{-1}$. The tensile strength of these films (20 μm thick) were measured to be 300–500 kg cm^{-2} . These values were much higher than those of some widely used engineering plastics such as poly(propylene) (260 kg cm^{-2})

and poly(vinyl acetate) (300 kg cm^{-2}).¹⁶ The monomer concentration and TFA content in the mixed electrolyte have strong affections on the mechanical properties of the PPP films. High concentration and high content TFA result in high polymerization rate and porous film. On the other hand, low TFA content leads high oxidation potential of the monomer, which may cause degradation of the polymer. The highest quality PPP film was obtained from the optimum condition of 0.3 M benzene in BFEE mixed with 33% TFA solution. The tensile strength of this film (20 μm) was measured to be $770 \pm 50 \text{ kg cm}^{-2}$ at a stretching rate of 0.5 cm min^{-1} , and its elongation at break was about $1.5 \pm 0.5\%$. This value is about 80% to that of an aluminum foil ($\sim 1000 \text{ kg cm}^{-2}$) and much higher than those for the PPP films obtained from other media.

Figure 5 presents the typical scanning electron microscopy images of the PPP film prepared at 1.7 V vs. SCE and by using BFEE containing 33% TFA as the electrolyte. These pictures showed that the morphologies of the two sides of the PPP film were different. The side contacted to the electrode is relatively flat and compact [Fig. 5(A)]. However, the side exposed to the solution is rough and irregular [Fig. 5(B)].

The thermal property of the PPP films was measured by thermogravimetric analysis (TGA) tests. According to the curves (Fig. 6), in the re-

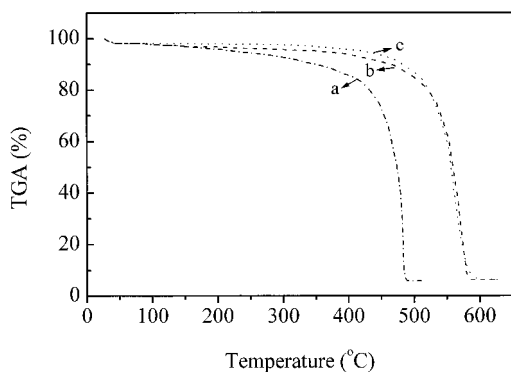


Figure 6 TGA curves of the PPP films obtained from the electrolytes of BFEE mixed with 15% (a), 33% (b), and 50% (c) TFA.

gion of 30–100°C, a weight loss lower than 5% was observed for these three samples, which should be due to the surface absorbed water.¹⁷ For sample A, in the 150–420°C region, there is a slow and continuous weight loss process, indicating a decomposition of low molecular weight oligomer.^{18,19} Above 420°C, the film undergoes a rapid decomposition of the polymer backbone and the weight loss is almost complete around 480°C. For samples B and C, no distinct decomposition of the films was found as the temperature increased up to about 450°C. However, above 490°C, samples B and C present a similar behavior, with onset of weight loss around 490°C and the loss is almost complete around 570°C, indicating that the films have a higher thermal stability.

CONCLUSIONS

In summary, high-quality free-standing PPP films can be prepared by the use of the mixtures of BFEE and TFA containing benzene as the electrolyte and a stainless steel sheet as the working electrode and at an applied potential of 1.7 V (vs. SCE). The films prepared under these conditions were shiny, flexible, and can be easily cut by conventional mechanical methods into a variety of structures. The film with highest quality was obtained from the system of 0.3 M benzene in BFEE mixed with 33% (by volume) TFA. The

tensile strength of this film was as high as $770 \pm 50 \text{ kg cm}^{-2}$, which was close to that of an aluminum foil. Furthermore, the PPP films have fairly high thermal stability and have many potential applications.

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