

# Preparation of a Porous Conducting Polymer Film by Electrochemical Synthesis–Solvent Extraction Method

Liang Li, Feng Yan, Gi Xue

*The State Key Lab of Coordination Chemistry, Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, China*

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**ABSTRACT:** Porous conducting polypyrrole (PPy) films have been obtained by electrochemical synthesis–solvent extraction method. The results of scanning electron microscopy (SEM) show that the size and the distribution of pores can be controlled during the electrochemical synthesis. The porous PPy films have sufficiently good mechanical properties, and electrochemical voltammetric studies imply that

the porous films also have high electrical conductivity and good electrochemical reversibility. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 303–307, 2004

**Key words:** polypyrrole; porous films; electrochemical synthesis; conducting polymers; electrochemistry; FTIR; SEM

## INTRODUCTION

During the past two decades, much interest has been generated in porous materials because of their great potential for applications in environment and industrial processes, such as reverse osmosis, ultrafiltration, and electrolysis.<sup>1–3</sup> Among them, numerous articles have been published which focused on the preparation of porous polymer materials.<sup>4–6</sup> Usually, organic porous polymer membrane can be generally prepared by immersion precipitation process or stretching method.<sup>3,6</sup> In the immersion precipitation method, a solvent-swollen thin film is suddenly immersed in a poor solvent for the polymer and then the solvent induces polymer chain shrinkage and pore formation. The pores can also be obtained by stretching a polymer thin film above the polymer transition temperature ( $T_g$ ) and then be stabilized by thermally quenching the film below  $T_g$ . Recently, the preparation of porous polymer materials by gel-casting and emulsion freeze-drying methods are also reported.<sup>7,8</sup> However, these methods only can be used to deal with polymer materials, which are either soluble or fusible, and cannot be conducted on some conjugate polymers. The main obstacle is that most conjugate polymers are both insoluble and infusible, such as polypyrrole (PPy) and polythiophene (PTh).

It has been reported that the conducting porous polymer materials could be widely used as electrode

material, electrolytic capacitors, and battery separators.<sup>9–11</sup> The preparation of porous conducting polymer has become an important branch of material research. Recently, several authors reported the chemical synthesis of porous conducting polymer films.<sup>12,13</sup> Koji et al. injected pyrrole monomer into the solvent-swollen polystyrene (PS) film and then subjected pyrrole monomer to polymerization and produced a PS/PPy composite film. After PS was extracted out from the solvent by some solvent, the porous conducting PPy film with a pore diameter of 0.1–100  $\mu\text{m}$  could be obtained.<sup>12</sup> Mitsuyuki prepared a porous composite membrane by the combination of PPy powder with a porous polypropylene film, which could be used to control ionic permeability.<sup>13</sup> However, in the process of the chemical synthesis, it was not easy to control the compatibility between two polymer phases. The mechanical properties and especially the conductivity of the porous films were often poor.

It is well known that the conducting PPy films synthesized through electrochemical method have high electrical conductivity and good environmental stability. Compared with the chemical synthesis, conducting porous polymer films prepared by electrochemical synthesis method would be more practicable. The key therefore to producing a porous PPy film by electrochemical synthesis method is to find a material which can be introduced to the PPy film during the process of electrochemical synthesis and also can be easily removed out from the PPy film after the electropolymerization.

It has been reported that some organic dyes such as methylene blue (MB) and indigo carmine (IC) had electrochemical activity and could be electroabsorbed or electropolymerized on some electrode surfaces under

Correspondence to: G. Xue (xuegi@nju.edu.cn).

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suitable conditions.<sup>14-16</sup> In addition, it has been found that MB monomer and its polymer can be easily dissolved in some suitable organic solvents. In this work, we prepared a porous film by electrochemical synthesis-solvent extraction method. PPy/MB composite film was electrochemically synthesized in the presence of MB solution. Then MB monomers were removed out from the film by extraction of some solvent, and thus, a porous conducting PPy film was obtained.

## EXPERIMENTAL

### Materials

Pyrrole monomer purchased from Aldrich was freshly distilled under nitrogen pressure before use. MB was used recrystallized from ethanol solution. Deionized and distilled water used throughout the work (Shanghai Reagent Co., China) was deprived of oxygen under a stream of nitrogen.

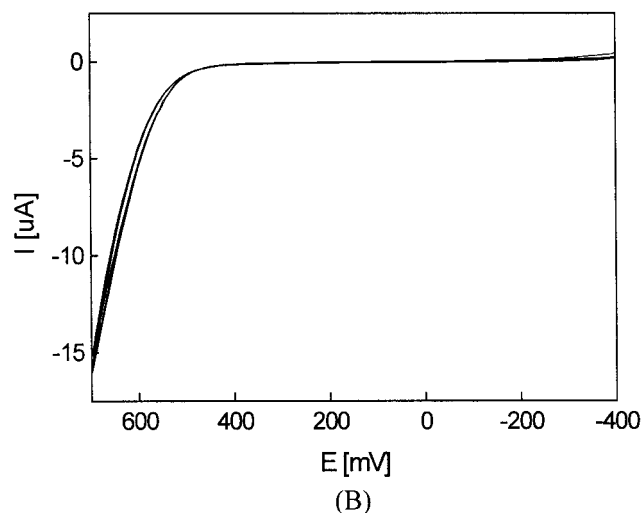
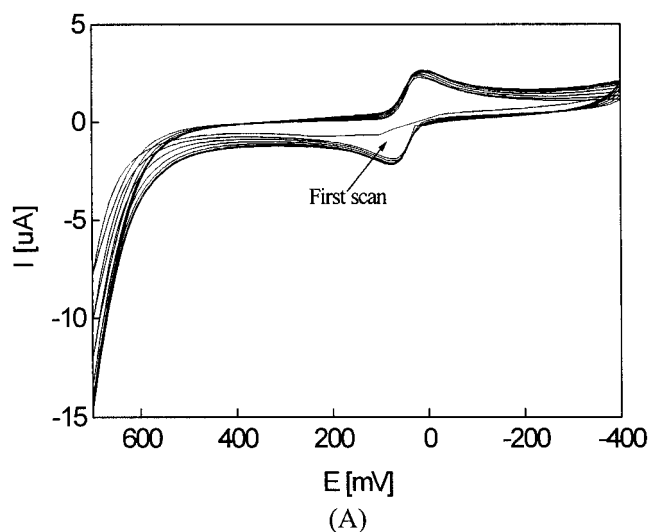
### Electrochemical experiments

The electrochemical synthesis of PPy/MB composite films was performed in a mixture of 0.1 mol/L pyrrole and  $2.5 \times 10^{-3}$  mol/L MB monomer aqueous solutions. Sodium dodecylbenzenesulfonate (SDBA; 0.1 mol/L) was used as the supporting electrolyte. Cyclic voltammetric experiments were performed in a traditional one-compartment three-electrode cell with the use of an EG&G potentiostat Model M273 under the control of a computer (Princeton Applied Research). Experiments were done at room temperature. Pt sheet and an Ag/AgCl (0.1 mol/L KCl) electrode were used as the counterelectrode and reference electrode, respectively. A Pt disc electrode ( $1.96 \times 10^{-3}$  cm<sup>2</sup>), which was polished with abrasive paper (1200 mesh) and diamond paste (1.5  $\mu$ m) and then washed with acetone, was used as the working electrode to investigate the cyclic voltammetric properties. A stainless sheet (1  $\times$  2 cm) was used as the working electrode to obtain a free-standing PPy/MB composite film, which was used in infrared spectroscopy investigation.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on an IFS-66V spectrometer (Bruker, Germany) under vacuum; the spectra were collected from 4000 to 400 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution over 50 scans. The PPy/MB composite films used in FTIR tests were peeled off the electrode and washed with distilled water and then dried under vacuum at ambient temperature for 24 h.

The PPy/MB composite film was extracted with acetone solution for 48 h and then dried under vacuum at ambient temperature for 24 h before conduc-



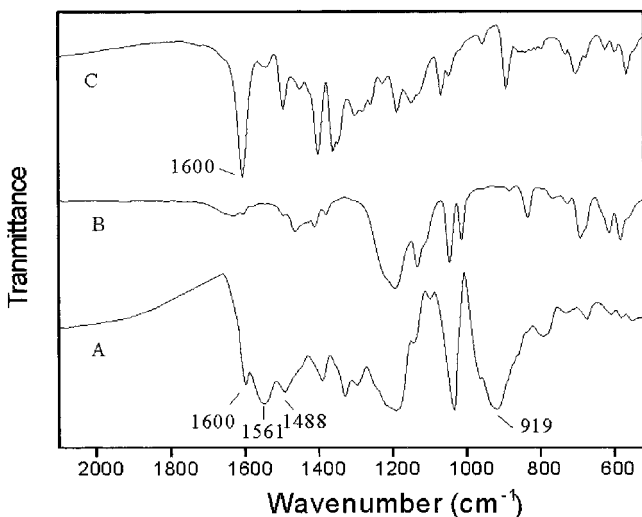
**Figure 1** Cyclic voltammograms of 0.1 mol/L pyrrole in the presence (A) and absence (B) of  $2.5 \times 10^{-3}$  mol/L MB monomer solutions on Pt electrode ( $1.96 \times 10^{-3}$  cm<sup>2</sup>). Scan rate: 50 MV/s; reference electrode: Ag/AgCl (0.1 mol/L KCl); supporting electrolyte: 0.1 mol/L SDBA solution.

tivity measurements. The conductivity of free-standing film was measured by conventional four-probe method under laboratory conditions. The surface morphologies of the porous polymer films were studied by taking scanning electron microscope (SEM) photographs from a Hitachi Model S570 SEM.

## RESULTS AND DISCUSSION

### Electrochemical preparation and characterization of porous PPy film

Figure 1 shows the cyclic voltammogram of pyrrole monomer in the presence and absence of MB aqueous



**Figure 2** Fourier transform infrared spectra of (A) as-prepared PPy/MB composite film; (B) supporting electrolyte SDBA and (C) MB.

solution. The electrochemical polymerization of PPy/MB composite film was investigated by cyclic voltammetry from  $-0.4$  to  $+0.7$  V versus Ag/AgCl ( $0.1$  mol/L KCl). It can be clearly seen from Figure 1(A) that the first voltammetric curve presents a rapid growth of the anodic current at about  $+0.55$  V, corresponding to the oxidation potential of pyrrole in Figure 1(B), implying that MB monomer does not affect the electropolymerization potential of pyrrole under these conditions. It has been reported that MB monomer could not be absorbed irreversibly on the bare metal electrode surfaces.<sup>15</sup> Thereby, no anodic peak of MB monomer is observed in the first anodic sweep. Once the electrode was covered with a layer of PPy film, MB monomer could be easily electrodeposited on the PPy film surface. A cathodic peak at about  $+0.015$  V was observed in the first cathodic scan and its corresponding oxidation peak at  $+0.070$  V also appeared in the second and successive anodic sweeps.<sup>15</sup> With an increase in the number of cycles, the anodic current intensities of pyrrole monomer increased steadily, indicating that PPy was growing on the electrode surface layer by layer. At the same time, more and more MB monomers were also absorbed on the PPy film to form electrochemical active layers, which led to an increase in the peak currents at  $+0.015$  and  $+0.070$  V. Because the polymerization reaction of poly(methylene blue) takes place only at fairly positive potential (amount to about  $+1.2$  V),<sup>14,15</sup> it can be supposed here that what were absorbed on the PPy film were mainly MB monomer.

The FTIR spectra of a blue-black PPy/MB composite film synthesized on a stainless steel sheet after 200 cycles were shown in Figure 2; the spectra of MB and SDBA were also offered for comparison. In Figure

2(A), characteristic absorption peaks of pyrrole ring at  $1561$  and  $1488$   $\text{cm}^{-1}$ , which were assigned to the C=C and C—C stretching vibration together with the C—H stretching vibration at  $919$   $\text{cm}^{-1}$ , can be clearly seen, indicating main components of composite film was polypyrrole.<sup>17–19</sup> Furthermore, another feature is an absorption band around  $1600$   $\text{cm}^{-1}$ , which is a characteristic band related to C=C and C=N stretching in the polyheterocycles,<sup>20</sup> as shown in Figure 2(C), suggesting that MB is absorbed on the PPy films.

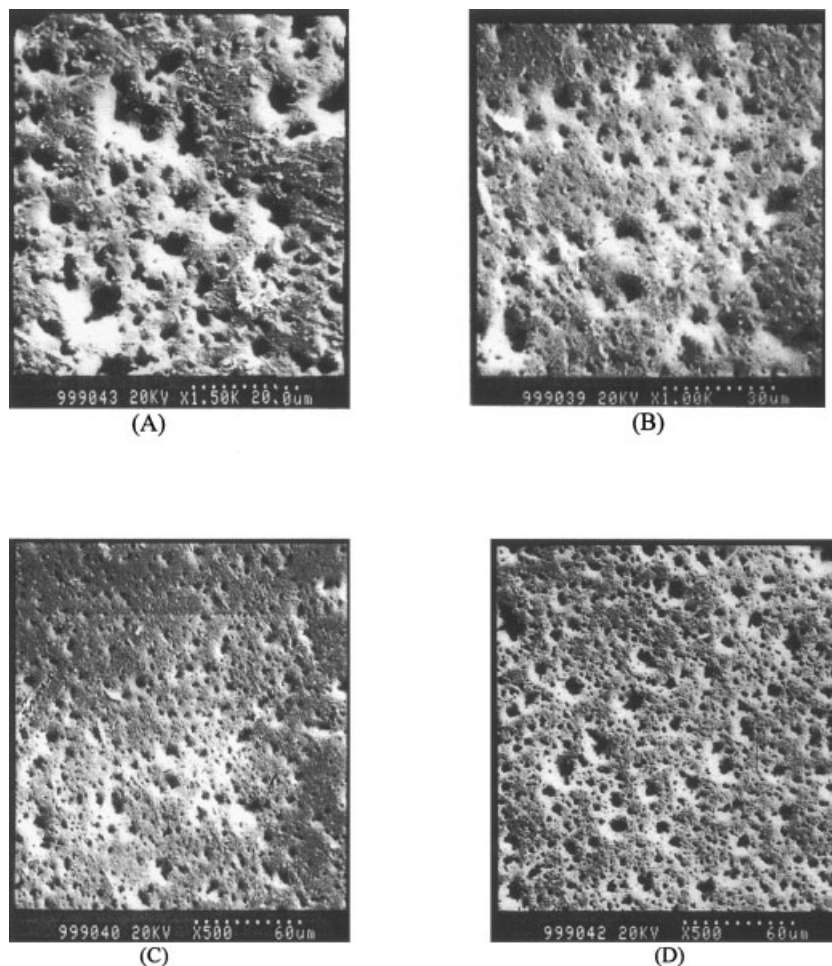
Figure 3 shows the SEM images of porous PPy film. As can be seen, the pores in this case have diameters of about  $1$ – $10$   $\mu\text{m}$ , and the size of the pores in the film changed with the cyclic scan speed. The higher the scan speed, the larger the sizes of MB particles in the film, and therefore, the resulting porous films have larger diameter pores. In addition, the concentration of MB monomer in the supporting electrolyte solution does not affect the formation of pores of the composite film. However, if the PPy film was produced in the absence of MB monomer by cyclic voltammetry, scanned in the MB aqueous solution in the range  $-0.4$  to  $+0.7$  V for 100 cyclic sweeps and extracted in the acetone solution for 48 h, a nodular or cauliflower-like surface morphology was found in the SEM of these PPy films (consistent with Bhattacharya et al.<sup>21</sup> and Prissanaroon et al.<sup>22</sup>) and no pores can be found in the SEM pictures.

Based on the above findings, it can be concluded that in the second electrochemical anodic sweep, some MB monomers began to be electrodeposited on the first layer of PPy film. This anodic sweep is a particle nucleation process of MB particles. In the successive anodic sweeps, MB monomers were electrodeposited earlier on the former MB particles to form larger particles.

### Mechanical and electrochemical properties of porous PPy films

The electrical and mechanical properties of porous PPy films electropolymerized by various scan rates are listed in Table I. As can be seen, the size and the distribution of pores were controlled by the cyclic scan speed. The lower the scan speed, the smaller the pore was formed. Additionally, the lower the scan speed, the more compact the PPy films; then the more compact film restricted the growth of MB particles. Therefore, the resulting porous films had smaller pores. However, when the scan speed is lower than  $10$  MV/s, the surface characteristics of conducting PPy film were almost unchanged and the diameter of pore almost unchanged too.

The porous film we prepared here has sufficiently good mechanical properties to be used as free-standing membranes. It is very flexible and can be cut like a metal sheet with a knife or a pair of scissors into



**Figure 3** Scanning electron microscopy images of porous PPy films obtained through cyclic voltammetry with different scan rate. (A) Growing surface of the film (scan rate 10 MV/s); (B) surface facing the electrode side (scan rate 10 MV/s); (C) growing surface of the film (scan rate 100 MV/s); (D) growing surface of the film (scan rate 200 MV/s).

various shapes. The highest tensile strength of the porous PPy film is measured to be 8.6 MPa at a stretching rate of 5 cm/min. The conductivity of free-standing PPy/MB composite film measured by conventional four-probe method is about 8.3 S/cm (electrochemical scan rate, 10 MV/s). However, after the extraction, the conductivity of the porous PPy film reaches about 46.7 S/cm; this value is lower than that of the pure PPy film, which may be attributed to the

**TABLE I**  
Electrical and Mechanical Properties of Porous PPy Films Electropolymerized by Various Scan Rates

Electrochemical scan rate (mV/s)	Diameter of pores ( $\mu\text{m}$ )	Conductivity (S/cm)	Tensile strength (MPa)
200	2–10	30.2	8
100	2–9	39.1	—
20	1–6	45.1	8.1
10	1–5	46.7	8.6
5	1–5	45.4	—

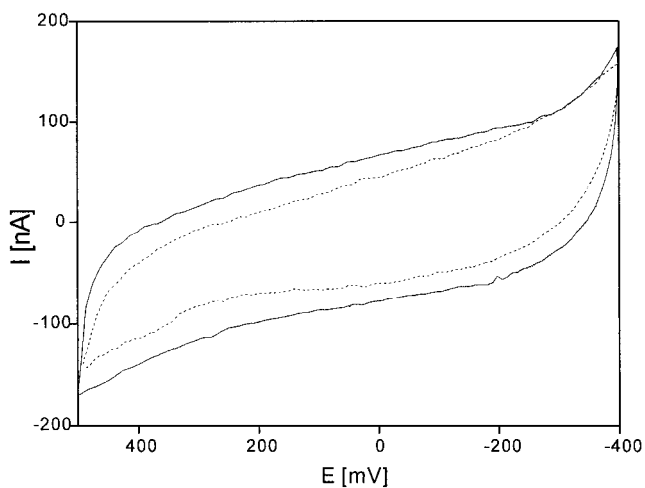
many micropores existing in the porous conducting PPy film.

If the obtained porous PPy electrode was scanned in 0.1 mol/L  $\text{LiClO}_4$  acetonitrile solution from  $-0.4$  to  $+0.7$  V for 100 cyclic sweeps,<sup>23</sup> about 78% of electrochemical activity was still maintained, indicating the conducting PPy film has good electrochemical reversibility (Fig. 4).

Because the film we synthesized contains some advantages mentioned above, further investigations on the applications of this porous PPy film are now in progress in our laboratory.

## CONCLUSION

In the preliminary work, we have described a method for the preparation of a porous conducting PPy film by the electrochemical synthesis–solvent extraction method. The result of electrochemical studies showed that the synthesized porous conducting PPy films have good electroactivity and electrochemical reversibility.



**Figure 4** Cyclic voltammograms of porous PPy film coated Pt electrode ( $1.96 \times 10^{-3} \text{ cm}^2$ ) in 0.1 mol/L  $\text{LiClO}_4$  acetonitrile solution. (—) The first scan; (---) the 100th scan. Scan rate: 20 MV/s.

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