

Electrochemical Properties of an Electrosynthesized Poly(*p*-phenylene vinylene) Film and Its Application to a Simple Electrochemical Fabrication of a Polymer Diode

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Cyclic voltammetry of a poly(*p*-phenylene vinylene) (PPV) film prepared by electrochemical reduction of  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene at Pt in THF shows an oxidation wave at *ca.* +0.8 V and a reduction wave at *ca.* -1.8 V vs. Ag/Ag<sup>+</sup> in 1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-MeCN. A polymer diode comprising cathodically polymerized PPV and anodically polymerized polypyrrole (PPy) can be fabricated by the simple one-pot electrochemical procedure.

In our previous paper has been described a simple method to synthesize free-standing films of PPV, which belongs to the family of organic conducting polymers.<sup>1)</sup> Our method utilizes electrochemical reduction of  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene in aprotic solvents. Although this method affords PPV with lower purity than the one prepared by the pyrolysis of a high molecular weight, water-soluble sulfonium salt precursor polymers,<sup>2)</sup> no need of heat treatment and faceteness in the synthetic procedure should be advantageous in applying to the construction of electrochemical devices such as polymer battery or diode. In this paper we present a first report on the electrochemical properties of the electrosynthesized PPV, showing reversible p- and n-type doping behaviors comparable with the chemically synthesized PPV. It has been reported that a direct contact between anion-doped and cation-doped conducting polymers acts as p-n junction, giving diode characteristics.<sup>3,4)</sup> A facile fabrication method of a polymer diode utilizing the electrosynthesized PPV and PPy is also demonstrated.

As has been reported, thick PPV films prepared electrochemically are apt to detach from the electrode surface.<sup>1)</sup> However, PPV films are adhesive to the electrode when they are prepared by constant potential electrolysis of 47 mmol dm<sup>-3</sup>  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene at -3.0 V vs. Ag/Ag<sup>+</sup> (10 mmol dm<sup>-3</sup> AgClO<sub>4</sub> in 0.1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NClO<sub>4</sub>-MeCN) at a platinum disk electrode in 3 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-THF with the amount of electricity less than 2 C cm<sup>-2</sup> (film thickness is less than 0.5  $\mu$ m). Cyclic voltammograms of PPV/Pt (prepared with 1 C cm<sup>-2</sup>) in 1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-MeCN are shown in Fig. 1. An oxidation wave appears from *ca.* +0.6 V when the potential is scanned in the positive direction, and the rereduction peak is seen at +0.65 V in the reverse scan. The potential sweep to the negative direction shows a reduction wave starting at *ca.* -1.8 V. The corresponding reoxidation wave at -1.93 V is negligible in size initially, but grows with increasing the scan number, and finally a steady-state quasi-reversible voltammogram is obtained. This might be because perchlorate ions which have been doped in the film during the previous oxidation and imperfect rereduction processes are dedoped simultaneously with the cation-doping reaction. The oxidation

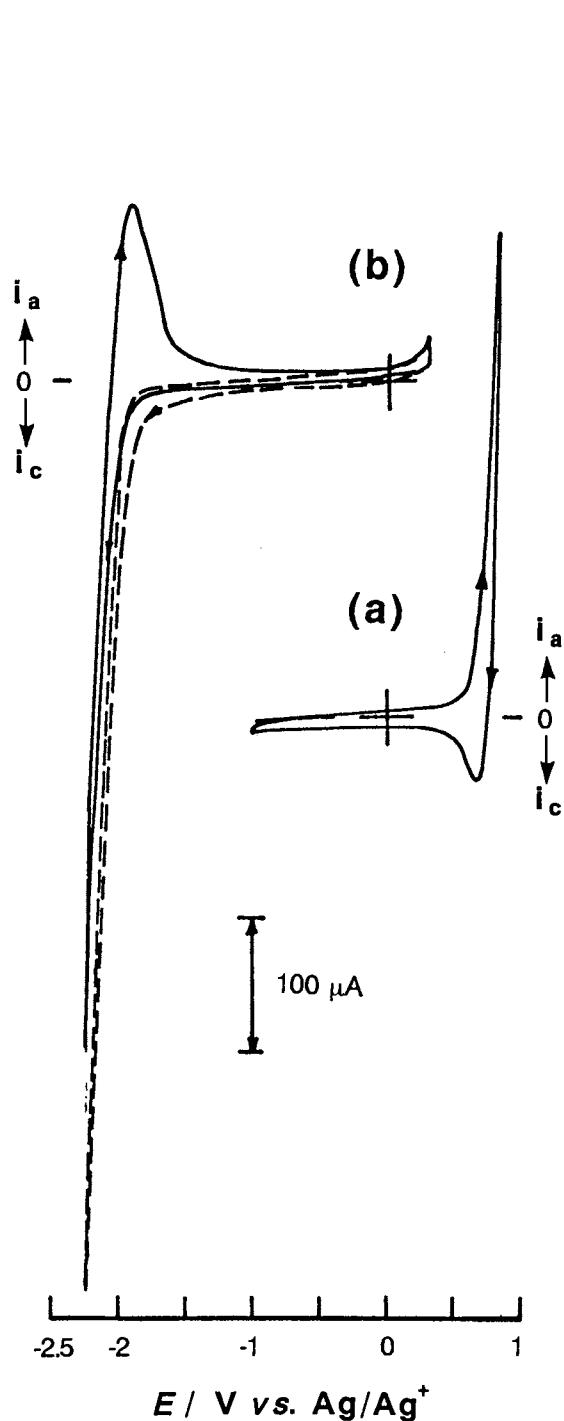


Fig. 1. Cyclic voltammograms of PPV/Pt in 1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NClO<sub>4</sub>-MeCN at a scan rate of 0.5 V s<sup>-1</sup>: (---) first scan, (—) steady state. Voltammogram (b) was obtained after recording (a).

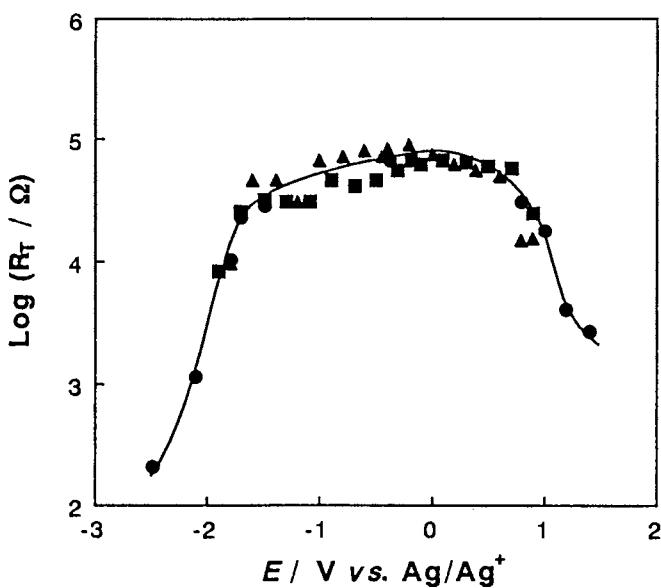


Fig. 2. Plots of  $R_T$  vs. electrode potential,  $E$ . Different marks indicate the results for different samples prepared under the same conditions given in the text.

and reduction potentials of the electrosynthesized PPV noted above are fairly in agreement with those of chemically synthesized PPV.<sup>5,6)</sup> The band gap calculated from the voltammogram in Fig. 1 is *ca.* 2.4 eV, consistent with the value obtained by spectroscopic<sup>6,7)</sup> and theoretical investigations.<sup>8)</sup>

A. c. impedance measurements were carried out for PPV/Pt in 1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-MeCN with changing the electrode potential. The charge-transfer resistance in the electrochemical redox process,  $R_T$ , was evaluated from the diameter of a semicircle in the Cole-Cole plots,<sup>9)</sup> and its dependency on the electrode potential is illustrated in Fig. 2. Decrease in  $R_T$  occurs in the potential range of both the anion and cation-doping processes as normally expected.<sup>9)</sup>

One-pot fabrication of a direct contact between PPV and PPy was made using a Au interdigitated (IDA) microelectrode with 50 fingers and a 15  $\mu$ m gap between the fingers<sup>4,10)</sup> and a solution of 25 mmol dm<sup>-3</sup>  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene and 100 mmol dm<sup>-3</sup> pyrrole in 0.1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-MeCN. The PPV film was firstly covered on half of the fingers by

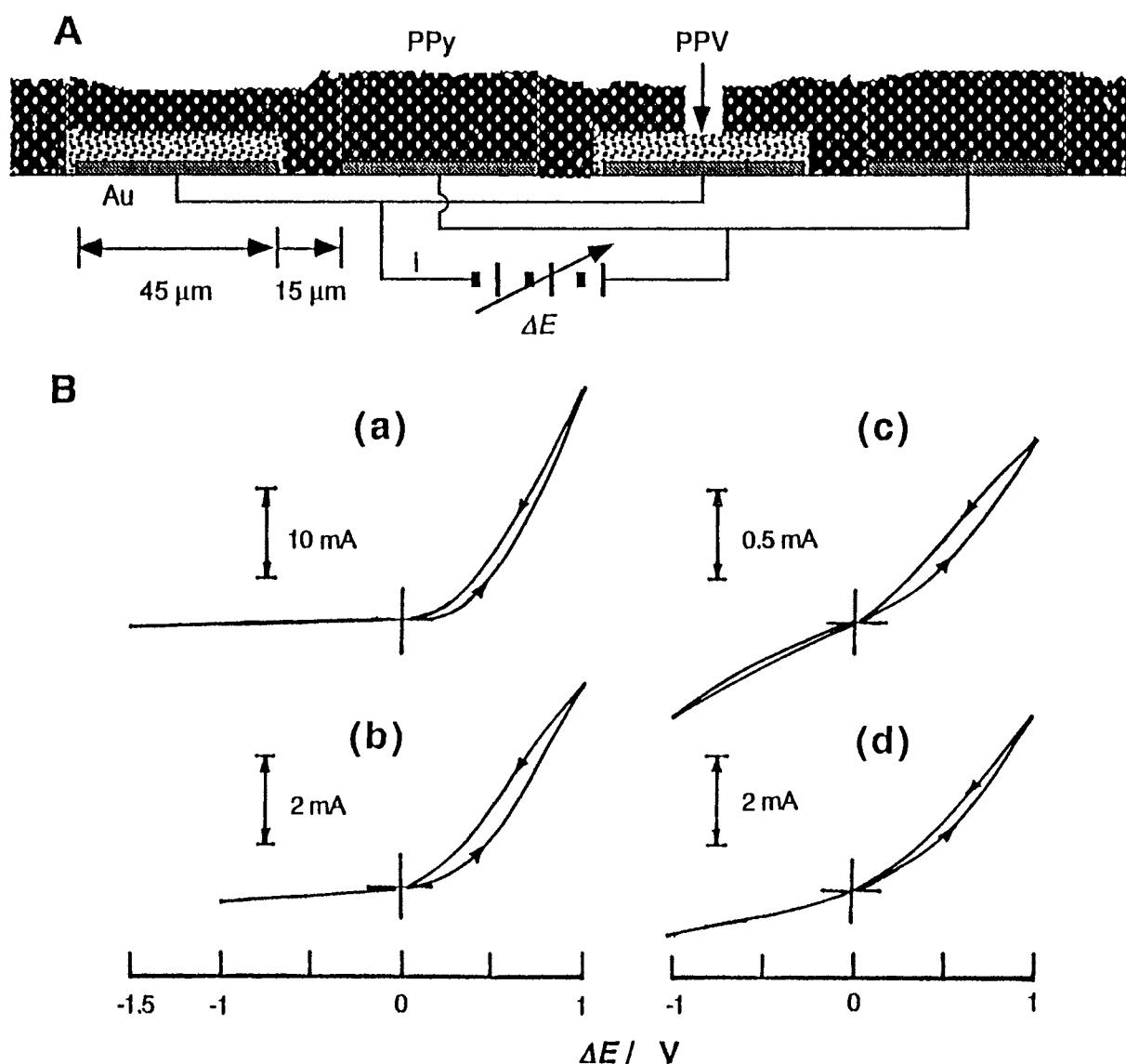


Fig. 3. (A) Structure of a PPV/PPy diode constructed on an IDA electrode. The vertical axis scale is expanded arbitrarily for visualization (thickness of Au fingers, PPV and PPy are approximately 100 nm, 100-200 nm and 10-30 μm, respectively. (B) Current-voltage characteristics of the diode: (a) in 0.1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-MeCN, (b) exposed to acetonitrile vapor, (c) under dry nitrogen, and (d) again exposed to acetonitrile vapor.

the controlled potential electrolysis at -2.7 V *vs.* Ag/Ag<sup>+</sup> for 120 s, then the PPy film prepared on other half fingers by the electrolysis at +1.1 V for 240 s. A rapid growth of PPy fills the gap between fingers, resulted in formation of direct contact between PPV and PPy (see Fig. 3A). Figure 3B represents the current-voltage characteristics of the device thus constructed. A diode characteristic is seen in 0.1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NBF<sub>4</sub>-MeCN and the direction of the current flow is consistent with the situation that PPV is an n-type semiconductor and PPy a p-type one. When the device is put out from the solution and exposed to the acetonitrile vapor, the diode characteristic is still maintained although the current decreases. The diode

behavior of the device becomes unclear when it is wholly dried (under  $N_2$ ), but recovers by exposing to acetonitrile vapor. This indicates that the ionic motion within PPV and/or PPy limits the charge conduction of the diode system.<sup>11)</sup> A detailed study on the charge-transport mechanism for the device is in progress.

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