

## Preparation and properties of polypyrrole

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### Abstract

Optimal conditions and improvement methods for electrochemical polymerization of pyrrole (Py) in the presence of sodium *p*-toluenesulfonate (PTS) as a dopant in water were studied. The electrical and spectral properties of poly-Py (PPy) doped with PTS were compared with those of PPy doped with sodium alkylbenzenesulfonates such as sodium benzenesulfonate (BS), sodium 4-ethylbenzenesulfonate (EBS), sodium 4-*n*-octylbenzenesulfonate (OBS), sodium dodecylbenzenesulfonate (DBS) and tetraethylammonium *p*-toluenesulfonate (Et<sub>4</sub>NPTS), prepared under the same polymerization conditions. UV-Vis-NIR absorption spectra were independent of the electrolytes used.

**keywords:** Electrochemical polymerization, UV-Vis-NIR absorption, Polypyrrole and derivatives

### 1. Introduction

Conducting polymers from five-membered heterocyclic compounds are very interesting. PPY[1] and polythiophene are typical examples. The electrochemical polymerization of Py in the presence of alkylbenzenesulfonates in water has been studied by many authors in order to improve the conductivity of PPy [2-6]. However, it is still important to find high-quality polymers and effective dopants showing more desirable properties. We have been systematically studying the preparation and properties of PPy derivatives doped with PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> in organic solvents [7]. In this paper we focus on optimal conditions and improvement methods for electrochemical polymerization of Py in the presence of bulky alkylbenzenesulfonates such as PTS, BS, EBS, OBS, DBS, sodium mesitylenesulfonate (MSS), sodium *m*-xylene-4-sulfonate (MXS) and Et<sub>4</sub>NPTS in water.

### 2. Experimental

Electrochemical polymerization was galvanostatically carried out at various current densities from 0.2 to 4 mA/cm<sup>2</sup> in deionised water in a nitrogen atmosphere. The anode was ITO and the cathode was a platinum plate. The charge passed during the polymerization was 1.2 C/cm<sup>2</sup>. PPy films were washed in water and acetonitrile, and then dried in a vacuum at 80°C for 1 h. Electrical conductivity measurements were performed using the usual four-probe method

on a Keithley 236 source measure unit and a 617 programmable electrometer. UV-Vis-NIR absorption spectra were recorded on a Hitachi U-3410 spectrophotometer. Cyclic voltammograms were measured at 0°C on a Hokuto Denko HA-501 potentiostat and a HB-105 function generator. For the absorption spectroscopy and cyclic voltammetry, thin films were prepared at 50 mC/cm<sup>2</sup> and 30 mC/cm<sup>2</sup>, respectively.

### 3. Results and discussion

To obtain high-quality polymer films by electrochemical polymerization, we first examined the effects of temperature, electrolyte, monomer concentration and current density on the conductivity of PPy doped with PTS. As a result, using Py concentrations of 0.1, 0.2 and 0.3 mol/l and electrolyte concentrations of 0.05, 0.1, and 0.2 - 1.0 mol/l, it was found that Py monomer and electrolyte concentrations of 0.2 and 0.3 mol/l, respectively, resulted in high conductivity. PPy films prepared at 0°C had a higher conductivity than films produced at -10, -5, 5, 10 and 15°C.

The conductivity increased with decreasing current density, but PPy was prepared as a heterogeneous film at a current density of 0.2 mA/cm<sup>2</sup>. A homogeneous film was obtained at a current density of 0.3 mA/cm<sup>2</sup>, and the maximum conductivity was 160 S/cm. The results of the electrochemical polymerization of Py are summarized in Table 1. When OBS and DBS were used, the reaction solutions were frozen during the polymerization. The films obtained were

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Table 1 Conductivity results

Nos.	Electrolyte	Solvent	Thickness ( $\mu\text{m}$ )	Conductivity (S/cm)
1	BS	H <sub>2</sub> O	4	110
2	PTS	H <sub>2</sub> O	4	160
3	EBS	H <sub>2</sub> O	4	140
4	MXS	H <sub>2</sub> O	4	80
5	MSS	H <sub>2</sub> O	4	50
6	OBS	H <sub>2</sub> O	20	16
7	DBS	H <sub>2</sub> O	7	14
8	Et <sub>4</sub> NPTS	H <sub>2</sub> O	4	110
9	Et <sub>4</sub> NPTS	CH <sub>3</sub> CN	5	90

Current density: 0.3 mA/cm<sup>2</sup>, Charge density: 1.2 C/cm<sup>2</sup>, Temperature: 0°C

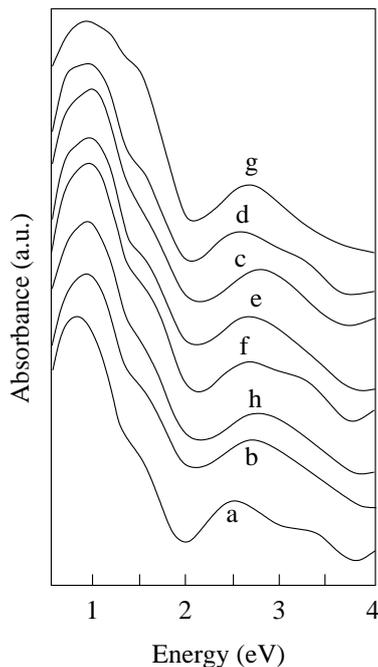


Fig. 2. UV-Vis-NIR absorption spectra of as-grown PPy films doped with BS(a), PTS(b), EBS(c), MXS(d), MSS(e), OBS(f), DBS(g) and Et<sub>4</sub>NPTS(h). Charge density: 50 mC/cm<sup>2</sup>.

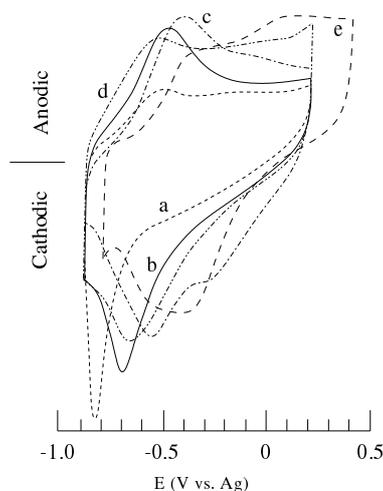


Fig. 3. Cyclic voltammograms of PPy films doped with BS(a), PTS(b), EBS(c), OBS(d) and DBS(e). Charge density: 30 mC/cm<sup>2</sup>, Sweep rate: 100 mV/sec.

heterogeneous and had low conductivities. Sodium alkylbenzenesulfonates were effective electrolytes for the electrochemical polymerization of PPy. In particular, PTS was a good electrolyte for use in the formation of the homogeneous conducting polymer films.

Fig. 2 shows the UV-Vis-NIR absorption spectra of as-grown PPy films doped with various dopants. The spectra shown in (a) to (h) have very similar shapes. Yakushi et al. have recorded the optical spectra of PPy at various stages of oxidation, from an as-grown highly oxidized film to an almost neutral film. In fully oxidized PPy, two broad bands are present at 1.0 and 2.7 eV and the interband transition appears as a shoulder at 3.6 eV (bipolaron formation) [8,9]. Each spectrum in figure 2 has the well-defined features of a bipolaron formation, showing the film to be in a fully doped state. It was found that the absorption spectra of the as-grown PPy films were independent of the electrolytes used.

Fig. 3 shows the cyclic voltammograms (CV) of PPy doped with various dopants. Ohtani et al. have reported that the transport of anions in a polymer body during oxidation or reduction depends greatly on the anion species. Smaller anions such as Cl<sup>-</sup> or BF<sub>4</sub><sup>-</sup> are omitted from the polymer in the oxidation state by reduction [7] while polyanions used as dopants in the polymerization stick to the polymer even during a vigorous reduction process [10]. The alkyl chain length of dopant anions used in CV measurement does not influence the oxidation peak potentials, but does influence the reduction peak potentials at a given sweep rate.

The results show that alkylbenzenesulfonates (0.3 mol/l) such as PTS and EBS were effective electrolytes for the polymerization of Py (0.2 mol/l) at a temperature of 0°C and a current density of 0.3 mA/cm<sup>2</sup>.

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