

# The Role of the Counter-ion during Magneto-electropolymerization of Polypyrrole-based Films

Hiroyuki Morioka, Tsunehisa Kimura and Ryoichi Aogaki\*

Department of Applied Chemistry, Faculty of Engineering, Tokyo Metropolitan University,  
1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, JAPAN

Fax: 81-426-77-2821, e-mail: morisan@ecomp.metro-u.ac.jp

\*Department of Product Design, Polytechnic University,

4-1-1 Hashimoto-dai, Sagami-hara, Kanagawa 229-1196, JAPAN

Fax: 81-427-63-9219, e-mail: aogaki@uitech.ac.jp

Electropolymerization under a magnetic field (magneto-electropolymerization) is a promising method to improve the structure and the physical property of conductive polymers. It is well known that pyrrole rings electropolymerized under the presence of anisotropic counter-ion having aromatic rings tend to lie preferentially parallel to the electrode surface. In the previous work, we have shown that the parallel orientation of this layer is reduced if a magnetic field is applied during electropolymerization in the direction parallel to the electric field, i.e., the direction perpendicular to the electrode surface. This is due to the diamagnetic anisotropy of layered structure. In this paper, we examine the effect of counter-ion and the resultant properties. Two different dopants, anisotropic and isotropic dopants, were used for the purpose. The magnetic fields were applied parallel to the faradic current to separate magnetohydrodynamic effect from the effect of magnetic field on alignment of the PPy layer. The analyses of the bulk structure and the cyclic voltammograms were carried out.

Key words: magnetic field, polypyrrole, magneto-electropolymerization, magnetic alignment

## 1. INTRODUCTION

Polypyrrole (PPy) film has drawn attention because of its good environmental stability and relatively high electrical conductivity. If a perfect molecular alignment is attained, the electrical conductivity parallel to the chain direction is up to 100 times larger than that in the transverse direction [1,2].

It is well known that *p*-toluenesulfonate-doped polypyrrole (PPy/TsO) film and 2-naphthalenesulfonate-doped polypyrrole (PPy/NS) film have a large anisotropic organization with layered structures of the aromatic rings parallel to the electrode surface while perchlorate-doped polypyrrole (PPy/ClO<sub>4</sub>) film and tetrafluoroborate-doped polypyrrole (PPy/BF<sub>4</sub>) film have an isotropic organization [3-5].

Magneto-electropolymerization (electropolymerization in magnetic field) is an interesting method to control the bulk structure, the surface morphology, and the redox behavior of PPy/TsO film [6-8] because the magnetic field affects on polymerization process through anisotropic diamagnetic susceptibility of PPy/TsO. Mogi et al. reported the magnetic field effects on the fractal growth morphology of electropolymerized conductive polymers [9,10], and the redox behavior of the magneto-electropolymerized film [11].

In this paper, we show that the magnetic effects on the redox behavior of PPy films are caused by the magnetic alignment of anisotropic organization occurring during magneto-electropolymerization. Two different dopants, anisotropic (TsONa, NSNa) and isotropic (NaClO<sub>4</sub>, NaBF<sub>4</sub>) dopants, were used for the purpose. The analyses of the bulk structure and the cyclic voltammograms were carried out.

## 2. EXPERIMENTAL

All chemicals were of guaranteed reagent grade. The PPy films were prepared by electrochemical oxidation of pyrrole monomer. The electrochemical polymerization reactions were carried out using a three-compartment cell in conjunction with a Toho Technical Research (TTR) 2000 potentiostat/galvanostat equipped with a TTR FG-02E function generator and personal computer under a nitrogen atmosphere. The PPy films were polymerized under a constant potential of 1.0 V in 0.1 M (1 M = 1 mol.dm<sup>-3</sup>) pyrrole aqueous solution until reaching a fixed charge (0.2 ~ 5.0 C.cm<sup>-2</sup>). Electrolytes were in most cases 0.1 M in both pyrrole and supporting electrolyte. All potentials were measured with respect to the Ag/AgCl electrode.

The magnetic fields were applied parallel to the faradic current to separate magnetohydrodynamic (MHD) effect [12] from the effect of magnetic field on alignment of the PPy layer. The MHD convection disturbs the film organization when prepared in the perpendicular condition [13]. The electrochemical cell was placed in the center of the liquid-helium-less superconducting magnet (Sumitomo Heavy Industries Ltd., HF10-100VHT), and the temperature was controlled to be at 20°C by using a water-circulating thermoregulator.

Cyclic voltammetric studies were performed using a computer-controlled electrochemical system (BAS 100B/W). The CV's of the PPy films were measured in aqueous solution containing 0.1 M supporting electrolyte. A platinum disk ( $\phi$  2.0 mm) was used as the working electrode and a platinum plate as the counter electrode.

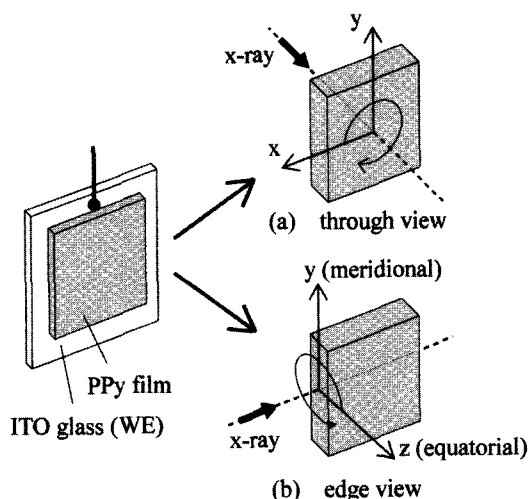


Fig. 1 The X-ray scattering geometry.

Wide-angle X-ray diffraction measurements were carried out with a MAC Science M18XHF-SRA equipped with an imaging plate, as shown in Fig. 1. An indium tin oxide glass electrode (ITO,  $30 \Omega/\square$ ,  $1 \times 1 \text{ cm}^2$ ) was used as the working electrode.

### 3. RESULTS AND DISCUSSION

Fig. 2 shows the CV's of the PPy/TsO films in a 0.1 M TsONa aqueous solution in the absence of magnetic field. The PPy/TsO films were polymerized in 0 T (0 T-PPy/TsO film) and 8 T (8 T-PPy/TsO film), respectively. A characteristic reduction peak at  $-440 \text{ mV}$  in the 0 T-PPy/TsO film shifts to a more negative potential of  $-640 \text{ mV}$  in the 8 T-PPy/TsO film. The peak potential is shifted because the mobility of the dopant in 8 T-PPy/TsO film is reduced. Mogi et al. studied the magnetopolymerization effects on the redox behavior of PPy/TsO films and showed that at the reduction process both the anion undoping and the  $\text{Na}^+$  doping occur in the 0 T-PPy/TsO films, while the  $\text{Na}^+$  doping dominantly occurs in the magneto-electropolymerized films [14].

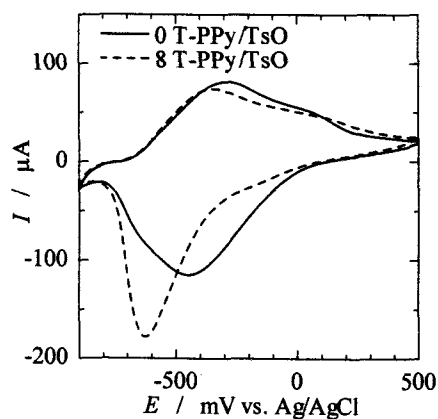


Fig. 2 Cyclic voltammograms of the PPy/TsO film ( $0.5 \text{ C.cm}^{-2}$ ) in a 0.1 M TsONa aqueous solution with a potential sweep rate of  $50 \text{ mV.s}^{-1}$  in the absence of a magnetic field.

The X-ray measurements were carried out on thicker films. In order to estimate the effect of the film thickness on the film structure, the cathodic peak potential was measured as a function of the quantity of electricity which is proportional to the film thickness. Fig. 3 shows that the cathodic peak potential remains unchanged irrespective of the thickness. Thus, it is allowed to discuss the X-ray results in relation to the electric analyses.

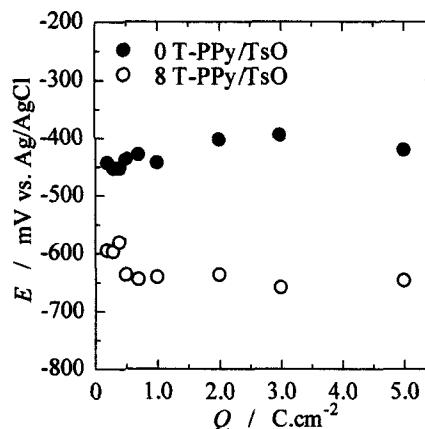


Fig. 3 The cathodic peak potentials in the CV's of the PPy/TsO film in a 0.1 M TsONa aqueous solution with a potential sweep rate of  $20 \text{ mV.s}^{-1}$  in the absence of a magnetic field.

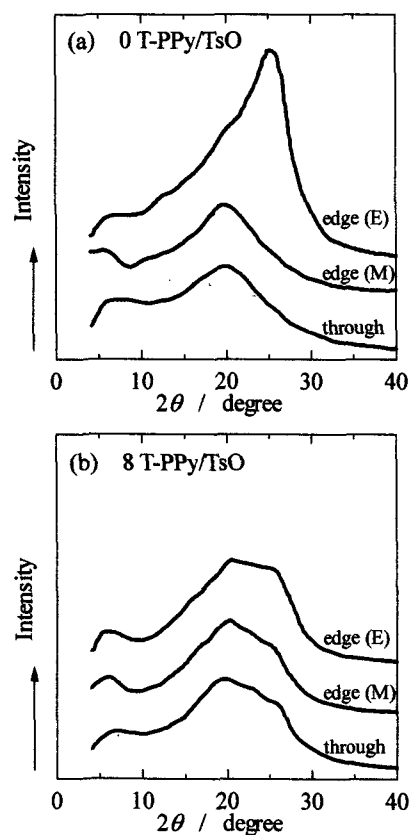


Fig. 4 X-ray scattering curves for PPy/TsO films electropolymerized in (a) 0 T and (b) 8 T. E; equatorial, M; meridional

Fig. 4 shows the wide angle X-ray diffraction pattern of PPy/TsO film electropolymerized in 0 T and 8 T. A peak around  $2\theta = 25^\circ \sim 26^\circ$  is attributed to the diffraction due to the spacing between pyrrole rings [15,16]. In the absence of the magnetic field (Fig.4 (a)), the edge view (equatorial) exhibits a maximum around  $2\theta = 25^\circ \sim 26^\circ$  region, indicating a parallel alignment of the layered structure with respect to the electrode surface. In Fig. 4 (b), the peak around  $2\theta = 25^\circ \sim 26^\circ$  region is weaker in the edge view (equatorial) and more intense in the through view than that observed for the 0 T-PPy/TsO shown in Fig.4 (a). This observation indicates that the tendency of the PPy to form a layered structure is partially suppressed by the application of the magnetic field. This is due to the diamagnetic anisotropy of the pyrrole ring that makes the pyrrole rings to align parallel to the field, that is, perpendicular to the electrode.

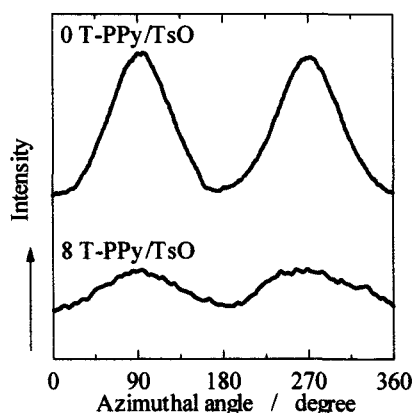


Fig. 5 X-ray azimuthal scans along pyrrole rings of PPy/TsO films electropolymerized in 0 T and 8 T.

Fig. 5 shows the wide-angle X-ray azimuthal scans carried out for the edge view at  $2\theta = 26^\circ$  for PPy/TsO films. The angles  $0^\circ$ ,  $180^\circ$  and  $360^\circ$  correspond to the direction of the magnetic field. Peaks at  $90^\circ$  and  $270^\circ$  indicate the parallel alignment of the layered structure of PPy. It is obvious that the parallel alignment is suppressed by the application of the magnetic field.

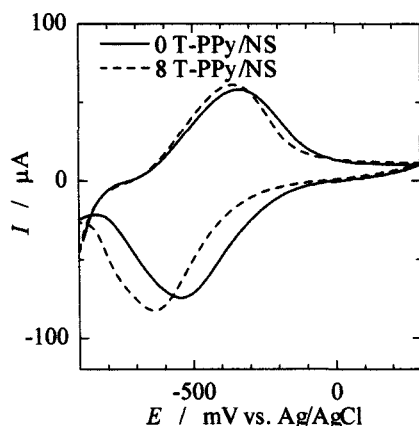


Fig. 6 Cyclic voltammograms of the PPy/NS film ( $0.3 \text{ C.cm}^{-2}$ ) in a 0.1 M NSNa aqueous solution with a potential sweep rate of  $50 \text{ mV.s}^{-1}$  in the absence of a magnetic field.

Fig. 6 shows the CV's of the PPy/NS films in a 0.1 M NSNa aqueous solution in the absence of a magnetic field. A characteristic reduction peak at  $-530 \text{ mV}$  in the 0 T-PPy/NS film shifts to a more negative potential of  $-650 \text{ mV}$  in the 8 T-PPy/NS film.

Fig. 7 shows the wide-angle X-ray azimuthal scans carried out for the edge view at  $2\theta = 26^\circ$  for PPy/NS films. Here we also observe the effect of magnetic field on the reduction of the layered structure. The tendency of PPy to align on the electrode surface is suppressed when a magnetic field is applied.

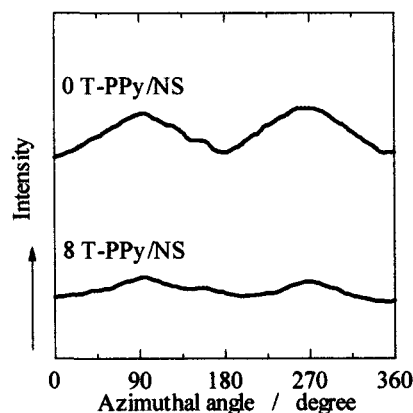


Fig. 7 X-ray azimuthal scans along pyrrole rings of PPy/NS films.

Fig. 8 shows the CV's of the PPy/ $\text{ClO}_4$  films in a 0.1 M  $\text{NaClO}_4$  aqueous solution in the absence of a magnetic field. No considerable difference is observed between 0 T- and 8 T-PPy/ $\text{ClO}_4$  films during the doping-undoping process.

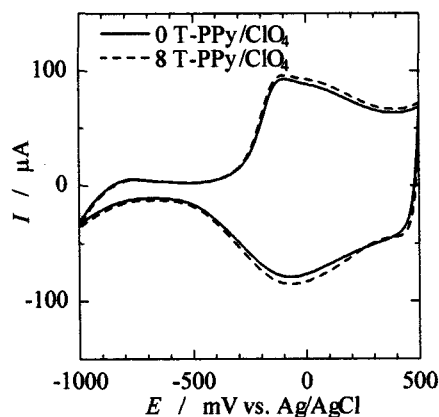


Fig. 8 Cyclic voltammograms of the PPy/ $\text{ClO}_4$  film ( $0.5 \text{ C.cm}^{-2}$ ) in a 0.1 M  $\text{NaClO}_4$  aqueous solution with a potential sweep rate of  $50 \text{ mV.s}^{-1}$  in the absence of a magnetic field.

Fig. 9 shows the wide-angle X-ray azimuthal scans carried out for the edge view at  $2\theta = 26^\circ$  for PPy/ $\text{ClO}_4$  films. Even the 0 T-PPy/ $\text{ClO}_4$  does not exhibit the layered organization. A similar result is obtained for the PPy film prepared with  $\text{BF}_4$ . The magnetoelectropolymerization does not affect the doping-undoping process nor molecular orientation in PPy/ $\text{BF}_4$ .

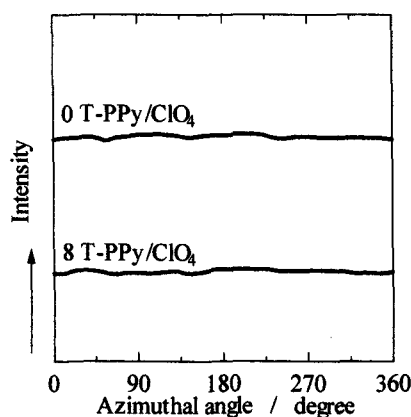


Fig. 9 X-ray azimuthal scans along pyrrole rings of PPy/ClO<sub>4</sub> films electropolymerized in 0 T and 8 T.

These observations, in comparison to the PPy/TsO and PPy/NS, indicate that molecular shape of the dopant plays an important role for the magnetic alignment of PPy during the magneto-electropolymerization. Anisotropic dopants (TsO, NS) encourage the alignment, while isotropic dopants (ClO<sub>4</sub>, BF<sub>4</sub>) do not. Since the anisotropic order is necessary for the magnetic alignment to occur, we might say that the isotropic dopants are unable to encourage the formation of the ordered structure necessary somewhere in the course of polymerization. This nature of the isotropic dopants is reflected on the observation that even without magnetic field no layered organization is formed on the electrode surface.

#### 4. CONCLUSIONS

We have shown that the PPy film structure strongly depends on the dopant used. Anisotropic dopants encourage the formation of anisotropic structures (probably the complex of the pyrrole and the dopant) during electropolymerization. In fact, even by polymerization without the magnetic field, PPy layered organizations, piled parallel to the electrode surface, are formed if the anisotropic dopants are used. Due to the anisotropic structures, the applied magnetic field works effectively during the electropolymerization, resulting in the reduction of the parallel piling of the layered organization. On the other hand, isotropic dopants are unable to form the anisotropic structures. As a result, no PPy layered structures are formed, nor is effective the applied magnetic field. It was found that there is good correlation between the alignment in the PPy film and the dopant mobility in the film.

#### References

- [1] J. H. Edwards, W. J. Feast and D. C. Bott, *Polymer*, **25**, 395-398 (1984).
- [2] H. Naarmann and N. Thephilou, *Synth. Met.*, **22**, 1-8 (1987).
- [3] G. R. Mitchell, *Polym. Commun.*, **12**, 346-349 (1986).

- [4] G. R. Mitchell, F. J. Davis and C. H. Legge, *Synth. Met.*, **26**, 247-257 (1988).
- [5] G. R. Mitchell, F. J. Davis and R. Cywinski, *Polym. Commun.*, **30**, 98-101 (1989).
- [6] I. Mogi, *Chem. Lett.*, **1996**, 419-420.
- [7] I. Mogi, K. Watanabe and M. Motokawa, *Electrochemistry*, **67**, 1051-1053 (1999).
- [8] I. Mogi, K. Watanabe and M. Motokawa, *Mat. Trans. JIM*, **41**, 966-969 (2000).
- [9] I. Mogi and M. Kamiko, *Bull. Chem. Soc. Jpn.*, **69**, 1889-1892 (1996).
- [10] I. Mogi and M. Kamiko, *Denki Kagaku (Presently Electrochemistry)*, **64**, 842-844 (1996).
- [11] I. Mogi, K. Watanabe and M. Motokawa, *J. Electroanal. Chem.*, **507**, 198-201 (2001).
- [12] R. Aogaki, K. Fueki and T. Mukaibo, *Denki Kagaku (Presently Electrochemistry)*, **43**, 504-508 (1975).
- [13] H. Morioka, T. Kimura and R. Aogaki, *Trans. Mat. Res. Soc. Jpn.*, **25**, 65-68 (2000).
- [14] I. Mogi and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **70**, 2337-2340 (1997).
- [15] K. J. Wynne and G. B. Street, *Macromolecules*, **18**, 2361-2368 (1985).
- [16] L. J. Buckley, D. K. Roylance and G. E. Wnek, *J. Polym. Sci. Polym. Phys. Ed.*, **25**, 2179-2188 (1987).

(Received December 21, 2001; Accepted January 30, 2002)