

Anion Dominated Electrochemical Process of Poly(*N*-methylpyrrole)

JIANYONG OUYANG and YONGFANG LI*

Institute of Chemistry, Academia Sinica, Beijing 100080, China

SYNOPSIS

The electrochemical behavior of poly(*N*-methylpyrrole) (PNMP) has been studied in aqueous solution by cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM). The electrochemical process of PNMP (TsO⁻) in TsONa solution or PNMP(NO₃⁻) in NaNO₃ solution showed good chemical reversibility. The process only involved the anion doping and dedoping. PNMP(TsO⁻) kept good electrochemical activity in NaNO₃ or Na₂SO₄ solution. But PNMP(NO₃⁻) became less active electrochemically in Na₂SO₄ solution and inactive in TsONa solution. PNMP(NO₃⁻) in NaCl solution showed similar electrochemical behavior to that in NiCl₂ solution. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polypyrrole (PPy) has attracted a great deal of attention in recent years due to many potential applications, such as secondary battery,¹ electrochromic display,² catalysts,³ and ion exchange.⁴ With the development of the study, attention has also been paid to its derivatives both from doing theoretical study and from seeking new applications.⁵⁻¹¹ Among these derivatives, poly(*N*-methylpyrrole) (PNMP) has been studied quite broadly.⁹⁻¹⁶ PNMP has the conductivity four orders of magnitude less than that of its parent,⁹ while the polymers of poly(β,β -dimethylpyrrole) has the conductivity of the same order of magnitude as polypyrrole.¹⁰ The difference is perhaps the result of the ruin of the chain planarity by the methyl group on nitrogen atom in PNMP. These demonstrate that the steric structure of the chains has a great effect on the conductivity of the low dimensional conductor as polypyrrole. The introduction of the methyl group on the nitrogen atom influences not only the conductivity but also the redox potential. A. F. Diaz et al. found that PNMP had higher redox potential than PPy and thought it was caused by the steric effect of methyl group on nitrogen atom.⁹

On the other hand, PNMP has been found to be a promising material in many aspects.¹²⁻¹⁶ For example, it is more advantageous than PPy as the electrode material in secondary battery due to its higher redox potential.¹² The apparent color change from brown to yellow of the PNMP film can be observed between the oxidized and the reduced states, so it may be a promising material in electrochromic display.¹³ These applications involve the ion doping and dedoping from the polymer film during the electrochemical process.

The electrochemical properties of PPy has been studied extensively.¹⁷⁻²³ Its electrochemical process has good reversibility for the small doping anions, such as NO₃⁻,^{17,18} but very poor reversibility for the large doping anions, such as TsO⁻.¹⁹ In some case, the electrochemical process involves the doping and dedoping of cations.^{18,20,21} The electrochemical properties of PNMP may be influenced by the methyl group on nitrogen atom so may show some difference with that of PPy. These stimulate us to study the electrochemical properties of PNMP.

EXPERIMENTAL

PNMP films were electrochemically polymerized at 0.80 V versus SCE on a Pt disc with the diameter of 3 mm or an Au disc with the diameter of 6 mm in an aqueous solution of 0.1 M *N*-methylpyrrole and

0.2M NaNO₃ or 0.2M TsONa. The pH value of the solutions was adjusted to pH 3 by adding corresponding acid solution. The charge consumed during the polymerization is 20 mC for the Pt disc and 40 mC for the Au disc.

Cyclic voltammetry (CV) was carried out using an EG&G PAR model 174A polarographic analyzer and Model 175 universal programmer with the Pt disc as the working electrode and a Pt plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A potential scan rate of 20 mV/s was used.

Recently, EQCM has been used to study the electrochemical behavior of the conducting polymer due to the accurate measurement of the film mass on the quartz crystal.^{20,21} In the EQCM experiments, frequency change was measured by ADVANTEST R5361 frequency counter. The Au disc deposited on the surface of a 5 MHz At-cut quartz was used as the working electrode in the EQCM study.

All potential in this paper referred to SCE.

RESULTS AND DISCUSSION

Electrochemical Behavior of PNMP

The cyclic voltammogram of the PNMP(TsO⁻) film was investigated in 0.2M TsONa aqueous solution of pH 3 by CV between -0.30 and 0.60V, as shown in Figure 1(a). Only one redox process is observed. The redox peaks are rather broad. The difference of the cathodic peak potential E_{p_c} (+0.23 V) and the anodic peak potential E_{p_a} (+0.36 V) is large (130 mV), presumably due to the slow rate of ion diffusion in the PNMP film. The second reduction scan repeats the first reduction scan very well, indicating good reversibility of dedoping and redoping.

The electrochemical process was also studied by EQCM on a Au electrode, as shown in Figure 1(b). The frequency of the quartz crystal monotonously increases during the reduction and decreases during the oxidation. These reveal that the mass of the PNMP(TsO⁻) film keeps decreasing during the reduction and keeps increasing during the oxidation, since the mass change (ΔM) and the frequency change (Δf) follow the Sauerbrey equation:²⁴

$$\Delta f = -(2f_0^2 \cdot \Delta M) / (\rho_q^{1/2} \mu_q^{1/2} A).$$

During the reduction, the mass loss of the PNMP film should be the result of dedoping of the counteranions from the polymer as below.

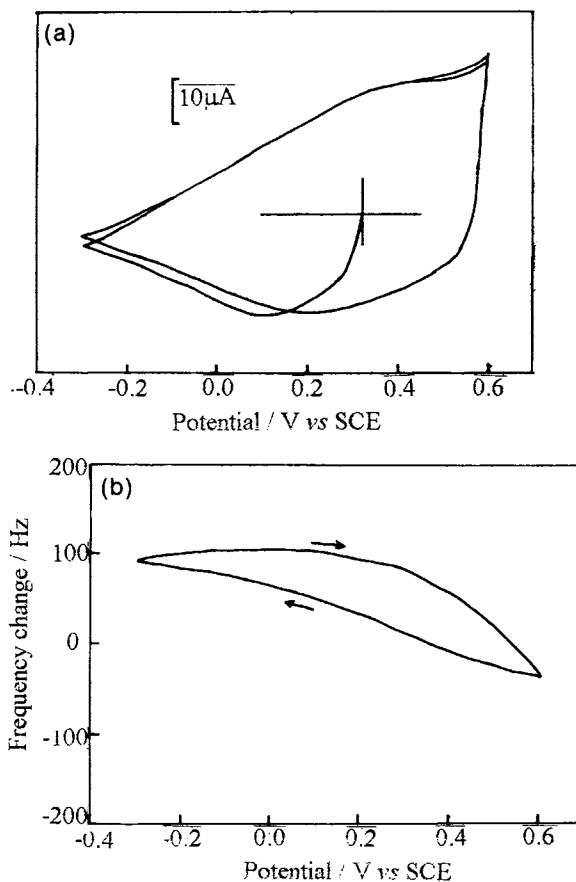
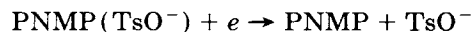
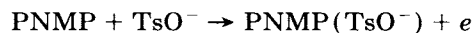


Figure 1 (a) Cyclic voltammogram of PNMP(TsO⁻) in 0.2M TsONa solution of pH 3 between -0.3 and +0.60V. (b) Frequency responses of PNMP(TsO⁻) in 0.2M TsONa solution of pH 3 between -0.3 and +0.60V.



Reversibly, the mass increase of the film during the oxidation is the result of the redoping of the counter anions into the polymer.



The monotonous mass change during the oxidation and the reduction indicates that the process only involves the anions doping and dedoping. After a complete cycle, the frequency of crystal returned to its original value, revealing that the amount of redoping anions equals to the amount of dedoping anions; that is, the process has good reversibility.

Analogous experiments were performed for the PNMP(NO₃⁻) film in aqueous 0.2M NaNO₃ solution of pH 3. Two anodic peaks were observed on the CV-gram (See Fig. 2). The anodic peak at 0.37 V is much stronger than the anodic peak at 0.0 V.

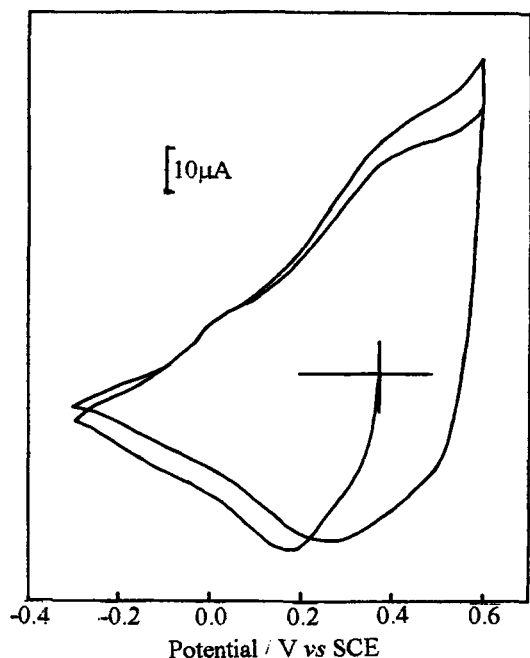


Figure 2 Cyclic voltammogram of PNMP (NO_3^-) in $0.2M$ NaNO_3 solution of pH 3 between -0.30 and $0.60V$.

The process also shows good reversibility. The process was studied by the EQCM experiments too, and results similar to that of PNMP(TsO^-) were observed.

From the above results, we can find that the redox potential of PNMP is higher than that of PPy,^{18,19} in agreement with the former result by A. F. Diaz.⁹ Another obvious difference between the electro-

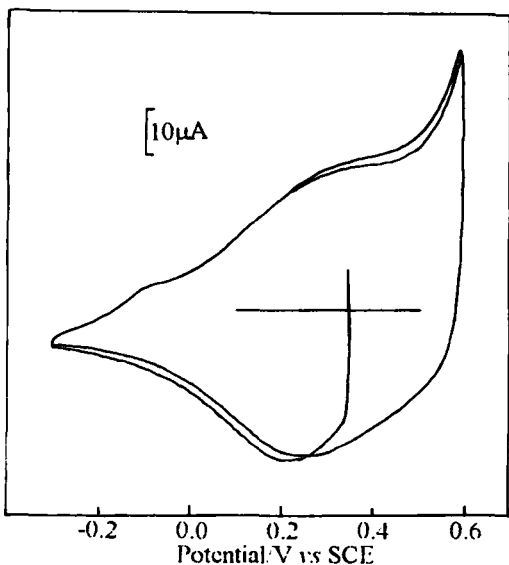


Figure 3 Cyclic voltammogram of PNMP (TsO^-) in $0.2M$ NaNO_3 neutral solution between -0.30 and $0.60V$.

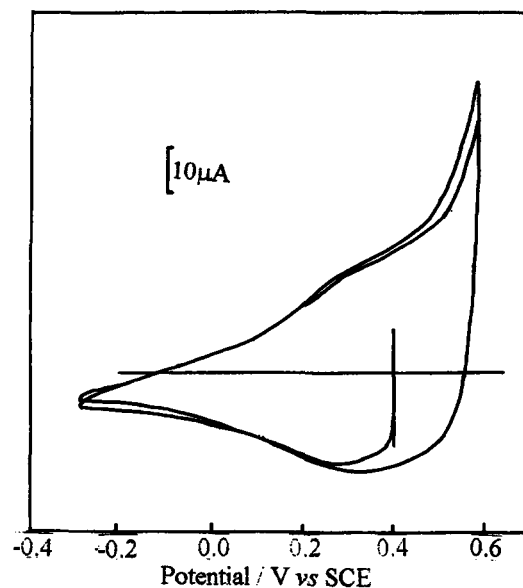


Figure 4 Cyclic voltammogram of PNMP (TsO^-) in $0.2M$ Na_2SO_4 solution of pH 3 between -0.30 and $0.60V$.

chemical behavior of PNMP and PPy is the redoping process. The electrochemical process of PNMP has good reversibility of dedoping and redoping not only for the small doping anions, such as NO_3^- , but also for the large doping anions, such as TsO^- . But PPy has good reversibility only for the small anions, such as NO_3^- .¹⁷⁻¹⁹ This should be the result of the steric effect of the methyl group on nitrogen atom in PNMP. Perhaps, the ion channel size is enlarged by the introduction of methyl group on nitrogen atom so that large anions TsO^- can transfer the PNMP film freely.

The mass change of PPy film doped by large anions is not monotonous, revealed by the EQCM experiments.^{20,21} During the reduction, the mass of the PPy film decreases at first and then increases. These are the results of the dedoping of anion at first and the intercalation of cation then.²¹ The EQCM ex-

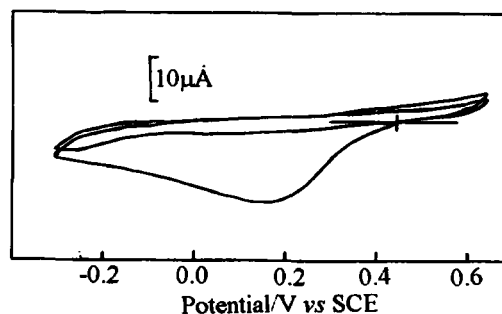


Figure 5 Cyclic voltammogram of PNMP (NO_3^-) in $0.2M$ TsONa neutral solution between -0.30 and $0.60V$.

periments of the PNMP film show that no doping of cations takes place.

Effect of Anions on the Electrochemical Behavior of PNMP

Further experiments were carried out to investigate the effect of anion in electrolyte on the electrochemical processes of PNMP. The cyclic voltammetry of a PNMP (TsO^-) film was performed in aqueous 0.2M NaNO_3 solution between -0.30 and 0.60V , as shown in Figure 3. The anions TsO^- are excluded from the polymer at the first reduction, and then the anions NO_3^- transfer into the polymer at the subsequent oxidation. The second reduction scan repeats the first one very well, indicating that PNMP (TsO^-) has good reversibility for the dedoping and redoping of NO_3^- anions in NaNO_3 solution. In Na_2SO_4 solution, PNMP (TsO^-) still has good reversibility during the electrochemical process (See Figure 4). These demonstrate that the polymer originally doped by the large-sized anions TsO^- is free for the doping of the middle-sized anions SO_4^{2-} and for the small-sized anions NO_3^- .

But when analogous experiments were performed for PNMP (NO_3^-) in TsONa or Na_2SO_4 solution, different results were observed. In TsONa solution, PNMP (NO_3^-) loses its electrochemical activity after the dedoping of NO_3^- at the first reduction (see Fig. 5). These reveal that the large anions as TsO^- cannot enter the PNMP originally doped by the small anions as NO_3^- . Less reversibility was observed for PNMP (NO_3^-) in Na_2SO_4 solution (see Fig. 6). These indicate that it is difficult for the middle-sized anions SO_4^{2-} to enter the PNMP (NO_3^-). From the above results, we can infer that the ion channel size

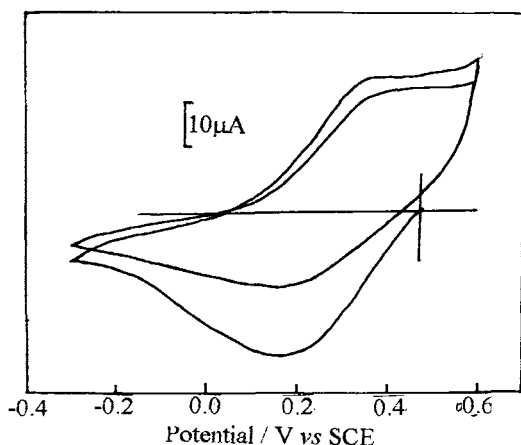


Figure 6 Cyclic voltammogram of PNMP (NO_3^-) in 0.2M Na_2SO_4 solution of pH 3 between -0.30 and 0.60V .

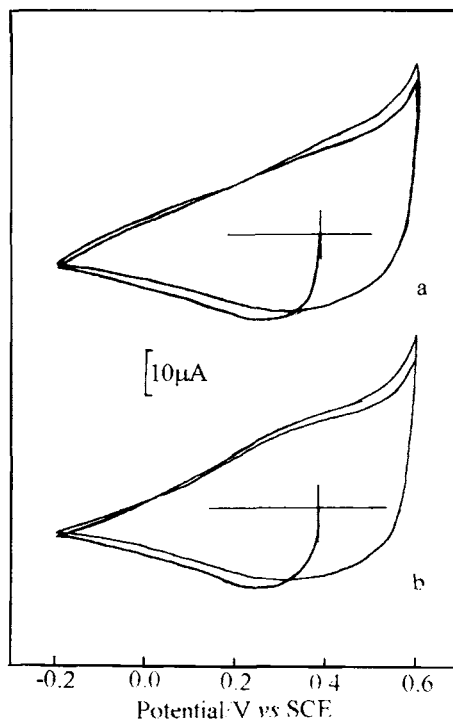


Figure 7 Cyclic voltammogram of PNMP (NO_3^-) between -0.30 and 0.60V in aqueous 0.2M NaCl neutral solution (a) and 0.1M NiCl_2 neutral solution (b).

in PNMP is determined by the originally doped anions.

Effect of Cations on the Electrochemical Behavior of PNMP

To investigate the influence of cation, the electrochemical switching of PNMP (NO_3^-) was carried out between -0.30 and 0.60V in aqueous 0.2M NaCl and 0.1M NiCl_2 neutral solution, as shown in Figure 7. They show similar electrochemical behavior, indicating that it is not related to the cations in solution. This is different from that of $\text{PPy}(\text{NO}_3^-)$. The electrochemical process of $\text{PPy}(\text{NO}_3^-)$ shows an obvious difference in the Na^+ and Ni^{2+} neutral solution.¹⁸

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