

# Effect of Electrolyte Concentration on the Properties of the Electropolymerized Polypyrrole Films

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**ABSTRACT:** The effect of electrolyte concentration on the electropolymerization of pyrrole was investigated by studies of conductivity, tensile strength, and absorption spectra, etc., of polypyrrole films prepared from electrolyte aqueous solutions. The electrolyte salts used in the studies include sodium *p*-toluenesulfonate (TsONa), NaClO<sub>4</sub>, NaNO<sub>3</sub>, and KCl. Cyclic voltammetry and elemental analysis were also performed in the studies of the effect of the NaNO<sub>3</sub> concentration. The conductivity, tensile strength, and the counteranion doping degree of conducting polypyrrole films increased obviously with increase of the electrolyte concentration of their polymerization solutions from 0.2 to 1 mol L<sup>-1</sup>. Further increase of the concentration over 1 mol L<sup>-1</sup> has a weak effect on the further improvement of the film quality of polypyrrole. So, 1 mol L<sup>-1</sup> was recommended for the electrolyte concentration of the polymerization aqueous solutions of pyrrole. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2739–2744, 1997

**Key words:** polypyrrole; electropolymerization; electrolyte concentration; conductivity; tensile strength

## INTRODUCTION

Conducting polypyrrole (PPy) has attracted much attention since Diaz et al. electropolymerized free-standing PPy films with a high conductivity of 10–100 S cm<sup>-1</sup> and good stability in air.<sup>1–3</sup> Among the studies performed on PPy, much effort has been devoted to its electrochemical preparation, including the polymerization mechanism and the optimization of the polymerization conditions such as electrolyte solvent, electrode material, supporting electrolyte anion, potential, current, and temperature to obtain flexible and highly con-

ductive PPy films. The most important factor to affect the polymerization is the nature of the electrolyte solutions used in the electrolysis. In the early stage of the study, Diaz et al. used a 0.06 mol L<sup>-1</sup> pyrrole and 0.1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub> acetonitrile solution containing 1% water.<sup>1</sup> The oxidation potential for pyrrole polymerization is in the range of 0.6–0.8 V versus SCE, which is lower than the electrolysis potential of water, so it was also performed in various aqueous solutions since 1984 in many laboratories.<sup>4–20</sup> The conductivity and morphology of PPy films strongly depend on the nature of the anions used in the electrolyte solutions.<sup>3,10–12</sup> More and more evidence has revealed that the solution anions take part in the polymerization processes.<sup>19,21</sup> So, the concentration of the electrolyte anions should play some role in the polymerization. The aqueous electrolyte solutions used are commonly composed of 0.1 mol L<sup>-1</sup> pyr-

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role and 0.1–0.2 mol L<sup>-1</sup> supporting electrolyte. The relatively low concentration of the supporting electrolyte in the aqueous solutions, selected by most researchers until now, may be affected by the study in the organic solutions. There is no reason to think that it is the best selection. Actually, the concentration effect on the conductivity of PPy was studied with TsONa as an electrolyte salt by Yoshino et al.<sup>8</sup> and Qian et al.<sup>13</sup> about 10 years ago. But it did not draw attention in the later studies on PPy preparation, and the concentration effect of other electrolyte salts except TsONa has not been studied yet. So, a deep study on the effect is necessary. In this article, the concentration effect on the physicochemical properties, such as conductivity, tensile strength, vis-NIR absorption spectra, and cyclic voltammetric property, of PPy films were studied for the electrolyte salts of TsONa, NaNO<sub>3</sub>, NaClO<sub>4</sub>, and KCl with their concentrations from 0.2 to 2 or 4 mol L<sup>-1</sup>. It was found that more flexible PPy films with a higher doping degree of counteranions and higher conductivity were obtained from aqueous solutions with higher electrolyte concentrations.

## EXPERIMENTAL

Electrochemical polymerization of pyrrole was performed in the aqueous solutions of 0.1 mol L<sup>-1</sup> pyrrole and 0.2–4 mol L<sup>-1</sup> NaNO<sub>3</sub>, NaClO<sub>4</sub>, and KCl or 0.2–2 mol L<sup>-1</sup> TsONa at a constant current of 1 mA cm<sup>-2</sup>. Pyrrole was distilled and preserved in an Ar atmosphere prior to use. The pH value of the solutions was adjusted to 3 by adding corresponding acid solutions. In the preparation of the PPy films for conductivity and mechanical property measurements, two stainless-steel plates were used as the anode and the cathode except that the ITO anode was used for the polymerization in KCl solutions. For the cyclic voltammetry, the PPy films were deposited on a Pt disc electrode with a 7 mm<sup>2</sup> area and 10 mC charge passed during its polymerization. For spectroscopy, the PPy films were produced on ITO electrodes.

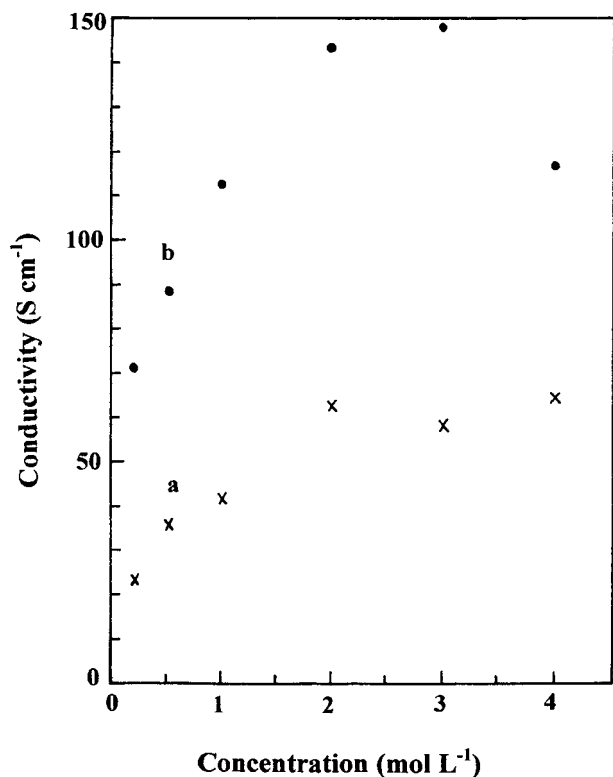
The conductivity of PPy films was measured by a four-probe method. Their tensile strength was determined at room temperature by an Instron 1122 universal testing instrument with a stretching rate of 1 mm/min. Cyclic voltammetry of PPy films was performed with an EG&G PAR Model 174A polarographic analyzer and a Model 175 universal programmer at a scan rate of 50 mV/s,

in a three-electrode cell with a Pt plate as the counterelectrode and a saturated calomel electrode (SCE) as the reference electrode. Vis-NIR absorption spectra were recorded on a Nanometrics Nanospec/10 microspectrophotometer.

## RESULTS AND DISCUSSION

### Conductivity

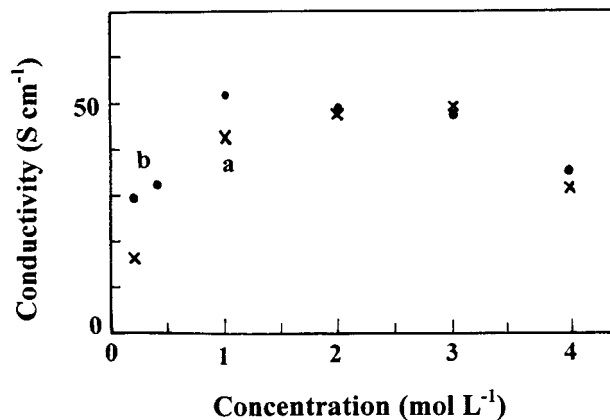
The conductivity and tensile strength are the most important properties of the conducting PPy films. The effect of electrolyte concentration on the conductivity of the as-prepared PPy films was studied first with the electrolytes of NaClO<sub>4</sub>, NaNO<sub>3</sub>, KCl, or TsONa. For NaClO<sub>4</sub>, the concentrations used in the electropolymerization solutions were 0.2, 0.5, 1, 2, 3, and 4 mol L<sup>-1</sup>. The electrochemical preparation of PPy(ClO<sub>4</sub><sup>-</sup>) was performed in the NaClO<sub>4</sub> aqueous solutions with 0.1 mol L<sup>-1</sup> pyrrole at -10°C. PPy films were deposited on both sides of the stainless-steel anode. The film on the anode surface facing the counterelectrode (film A) was thicker than that on the back surface of the anode (film B). The conductivity values of the films were strongly related to their film thickness. So, the conductivity of the films with similar thickness from the same side of the anode was compared here, as shown in Figure 1. The concentration has an obvious effect on the conductivity of the as-prepared PPy films when it was increased from 0.2 to 2 mol L<sup>-1</sup>. The conductivities of both films A and B obtained from the 2 mol L<sup>-1</sup> NaClO<sub>4</sub> solution are more than twice higher than those of the films deposited from the 0.2 mol L<sup>-1</sup> solution. But, further increase of the concentration seems to have no effect on the conductivity. It can also be seen from Figure 1 that the conductivity of film B from the 4 mol L<sup>-1</sup> electrolyte solution is lower than that from the 2 or 3 mol L<sup>-1</sup> solution, indicating that a too high concentration of the electrolyte may hinder the diffusion of pyrrole so that it affects negatively the conductivity of the as-prepared PPy film. In addition, the thickness dependence of the conductivity can also be seen from Figure 1, e.g., the conductivity of the film with the thickness of 7 μm from 2 mol L<sup>-1</sup> solution is 143 S cm<sup>-1</sup>, while it is 62 S cm<sup>-1</sup> for the film with the thickness of 12 μm. It should be noticed that the conductivity of the PPy(ClO<sub>4</sub><sup>-</sup>) film here is much higher than those in the literature for the films



**Figure 1**  $\text{NaClO}_4$  concentration dependence of the conductivity of the  $\text{PPy}(\text{ClO}_4^-)$  films prepared from pH 3,  $0.1 \text{ mol L}^{-1}$  pyrrole,  $\text{NaClO}_4$  aqueous solutions: (a) the films on the front side of the anode (the surface facing to the counter electrode) with the thickness of  $12\text{--}13 \mu\text{m}$ ; (b) the films on the back side of the anode with the thickness of  $6\text{--}8 \mu\text{m}$ .

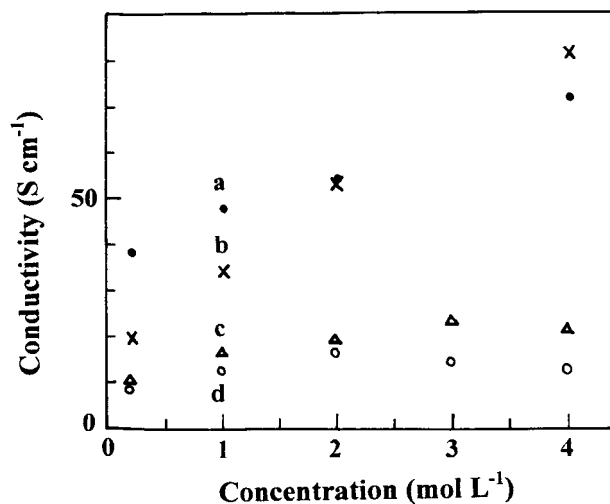
prepared from aqueous solutions, e.g., the conductivity of the  $\text{PPy}(\text{ClO}_4^-)$  film produced by Warren and Anderson is only  $4.9\text{--}6.5 \text{ S cm}^{-1}$ .<sup>12</sup> This indicates that the optimization of the polymerization conditions is very important for the preparation of highly conductive PPy films. The films here were produced at lower temperature ( $-10^\circ\text{C}$ ) in pH 3 aqueous solutions with higher electrolyte concentration ( $2 \text{ mol L}^{-1}$ ), while Warren and Anderson<sup>12</sup> prepared the  $\text{PPy}(\text{ClO}_4^-)$  films at room temperature in a strong acidic  $\text{HClO}_4$  solution with lower electrolyte concentration ( $0.1 \text{ mol L}^{-1}$ ).

A similar effect of the concentration on the conductivity of PPy films was also observed for the electrolyte salts of  $\text{NaNO}_3$  and  $\text{KCl}$ , as shown in Figures 2 and 3, respectively. Figures 2 and 3 display the temperature dependence of the polymerization as well. For the films prepared at a lower temperature of 0 or  $-10^\circ\text{C}$ , the higher the  $\text{NaNO}_3$  concentration of the polymerization solu-



**Figure 2**  $\text{KCl}$  concentration dependence of the conductivity of the  $\text{PPy}(\text{Cl}^-)$  films (on the front side of the anode) prepared from pH 3,  $0.1 \text{ mol L}^{-1}$  pyrrole,  $\text{KCl}$  aqueous solutions at (a) ( $\times$ )  $-10^\circ\text{C}$  and (b) ( $\bullet$ )  $0^\circ\text{C}$ ; the thickness of the films is ca.  $16\text{--}20 \mu\text{m}$ .

tions, the higher the conductivity of the  $\text{PPy}(\text{NO}_3^-)$  films obtained. Also, the films prepared at lower temperatures possess higher conductivity, which agrees with the literature.<sup>5,14,22,23</sup> For the electrolyte salt of  $\text{TsONa}$ , the conductivity of the PPy film (on the back side of the anode with  $7 \mu\text{m}$  thick) prepared at  $0^\circ\text{C}$  from  $1 \text{ mol L}^{-1}$   $\text{TsONa}$  is  $180.6 \text{ S cm}^{-1}$ , which is slightly higher than that of the PPy film ( $137.8 \text{ S cm}^{-1}$ ) produced from  $0.2 \text{ mol L}^{-1}$   $\text{TsONa}$  solution.



**Figure 3**  $\text{NaNO}_3$  concentration dependence of the conductivity of the  $\text{PPy}(\text{NO}_3^-)$  films (on the back side of the anode) prepared from pH 3,  $0.1 \text{ mol L}^{-1}$  pyrrole,  $\text{NaNO}_3$  aqueous solutions at (a) ( $\bullet$ )  $-10^\circ\text{C}$ ; (b) ( $\times$ )  $0^\circ\text{C}$ ; (c) ( $\Delta$ )  $10^\circ\text{C}$ ; and (d) ( $\circ$ )  $30^\circ\text{C}$ ; the thickness of the films is ca.  $6\text{--}9 \mu\text{m}$ .

**Table I** Tensile Strength (MPa) of the PPy Films (on the Front Side of the Anode) Prepared in pH 3, 0.1 mol L<sup>-1</sup> Pyrrole Aqueous Solutions with Various Electrolyte Concentrations of 0.2–4.0 mol L<sup>-1</sup>

Electrolyte Salts	Electrolyte Concentrations (mol L <sup>-1</sup> )					
	0.2	0.5	1.0	2.0	3.0	4.0
TsONa	43.8	54.2	73.8	56.9		
KCl	11.9		17.7	18.0	17.1	14.3
NaClO <sub>4</sub>	1.6	2.3	2.6	4.4	5.5	2.2
NaNO <sub>3</sub>	5.7		9.1	12.3		14.3

Thickness of the films is ca. 12–20  $\mu\text{m}$ .

### Tensile Strength

In addition to the effect on the conductivity of PPy, the concentration of the electrolyte also affects the tensile strength of the films prepared from the electrolyte solutions. The values of the tensile strength of the PPy films prepared from different electrolyte solutions with various concentrations are tabulated in Table I. It can be seen that the tensile strength of the PPy films prepared in 1 mol L<sup>-1</sup> electrolyte solutions increased by 50–70% as compared with those prepared from 0.2 mol L<sup>-1</sup> solutions for all the four electrolytes. At higher concentrations over 1 mol L<sup>-1</sup>, a weak effect of the electrolyte concentration on the mechanical property was demonstrated. So, 1 mol L<sup>-1</sup> should be the appropriate selection of the electrolyte concentration in a polymerization solution of pyrrole for the investigated supporting electrolyte salts.

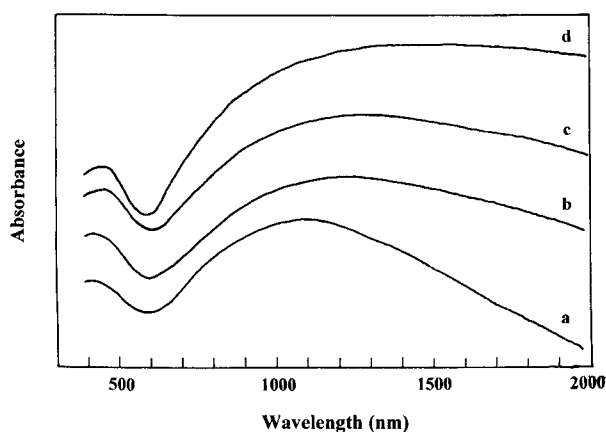
### Absorption Spectra

As mentioned above, increase of the electrolyte concentration has a positive effect on the conductivity and mechanical property of the PPy films. Naturally, one may consider what is the origin of the positive effect from the structural point of view. To investigate the structural characteristics, vis-NIR absorption spectroscopy was performed for the PPy films prepared from pH 3 aqueous solutions of 0.1 mol L<sup>-1</sup> pyrrole and various concentrations of NaNO<sub>3</sub>. The results are shown in Figure 4. The absorption peak in the NIR region increased and shifted to a longer wavelength with increase of the electrolyte concentration. The NIR absorption is related to the electron transition from the valence band to the bipolaron band of the conjugated chains of PPy,<sup>24</sup> i.e., related to the doping state of the conducting

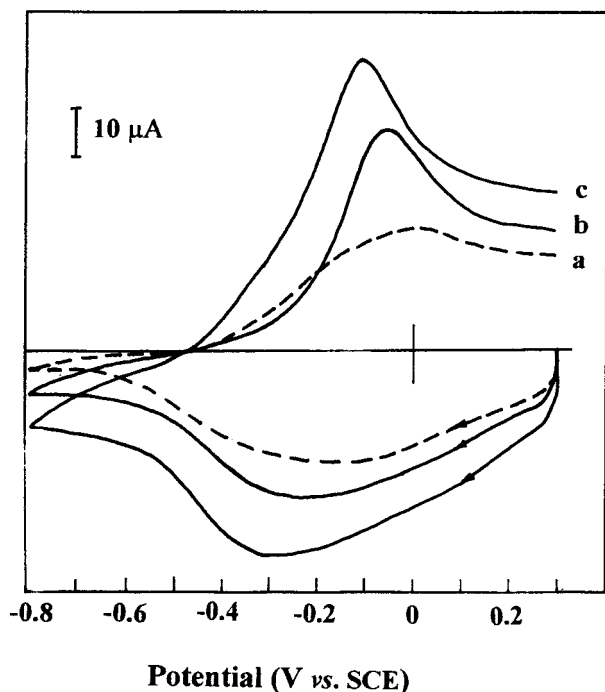
PPy and to the conjugation length of the PPy chain. So, the stronger NIR absorption indicates a higher counteranion doping degree, and the longer wavelength of the NIR absorption peak reveals the longer conjugation length of the PPy chain<sup>24</sup> prepared from the higher concentration solutions. These results are coincident with the conductivity and tensile strength measurements. The same tendency of the NIR absorption change with the electrolyte concentration was observed for the electrolytes of NaClO<sub>4</sub>, KCl, and TsONa.

### Cyclic Voltammograms

One of the authors has intensively studied the electrochemical properties of PPy(NO<sub>3</sub><sup>-</sup>) films by cyclic voltammetry.<sup>25</sup> It was found that the counteranion dedoped with the reduction of the PPy film in an acidic aqueous solution and the charge



**Figure 4** Vis-NIR absorption spectra of PPy(NO<sub>3</sub><sup>-</sup>) films prepared from pH 3, 0.1 mol L<sup>-1</sup> pyrrole aqueous solutions with various concentrations of NaNO<sub>3</sub>: (a) 0.01 mol L<sup>-1</sup>; (b) 0.05 mol L<sup>-1</sup>; (c) 0.2 mol L<sup>-1</sup>; (d) 5 mol L<sup>-1</sup>.



**Figure 5** Cyclic voltammograms of PPy( $\text{NO}_3^-$ ) films in pH 3,  $0.2 \text{ mol L}^{-1}$   $\text{NaNO}_3$  aqueous solution at  $50 \text{ mV/s}$ ; the PPy films were prepared from pH 3,  $0.1 \text{ mol L}^{-1}$  pyrrole aqueous solutions with various concentrations of  $\text{NaNO}_3$ : (a)  $0.05 \text{ mol L}^{-1}$ ; (b)  $0.2 \text{ mol L}^{-1}$ ; (c)  $5 \text{ mol L}^{-1}$ .

amount consumed in the reduction can be conveniently used to estimate its doping degree. To investigate the concentration effect on the electrochemical properties and on the doping degree of the as-prepared PPy films, a cyclic voltammetric measurement was carried out for the PPy( $\text{NO}_3^-$ ) film.

Figure 5 shows the cyclic voltammograms of the PPy( $\text{NO}_3^-$ ) films, prepared from pH 3,  $0.1 \text{ mol}$

$\text{L}^{-1}$  pyrrole aqueous solutions with (a)  $0.05 \text{ mol L}^{-1}$ , (b)  $0.2 \text{ mol L}^{-1}$ , and (c)  $5 \text{ mol L}^{-1}$   $\text{NaNO}_3$ , in pH 3,  $0.2 \text{ mol L}^{-1}$   $\text{NaNO}_3$  aqueous solution. Obviously, the reduction and reoxidation currents increased with increase of the electrolyte concentration. The reduction charge integrated from the cyclic voltammogram corresponds to the doping amount of the counteranions in the PPy film. So, the increase of the reduction current indicates that the doping degree of the counteranions in the PPy films from the  $5 \text{ mol L}^{-1}$  solution is much higher than that from  $0.05$  and  $0.2 \text{ mol L}^{-1}$  solutions. In addition, the redox potential of the PPy film prepared in the solution with higher electrolyte concentration shifted to lower potentials as compared with that prepared in the solution with lower electrolyte concentration. The reduction of PPy in the acidic solution is accompanied by the dedoping of its counteranions.<sup>25</sup> For example, the reduction potential of the film from the  $5 \text{ mol L}^{-1}$   $\text{NaNO}_3$  solution is  $-0.31 \text{ V}$  versus SCE, while that of the film from  $0.05 \text{ mol L}^{-1}$   $\text{NaNO}_3$  solution is  $-0.18 \text{ V}$  versus SCE. The negative shift of the redox potential implies that the conjugation length of the PPy from the  $5 \text{ mol L}^{-1}$   $\text{NaNO}_3$  solution is longer than that from  $0.05$  and  $0.2 \text{ mol L}^{-1}$   $\text{NaNO}_3$  solutions. These results agree with those of the NIR absorption spectra.

To confirm the higher doping degree of the PPy films from the solutions with higher electrolyte concentrations, elemental analysis was carried out for the PPy( $\text{NO}_3^-$ ) films from pH 3,  $0.1 \text{ mol L}^{-1}$  pyrrole aqueous solutions with different concentrations of  $\text{NaNO}_3$ . The results of the elemental analysis are listed in Table II. The doping degree of the counteranion  $\text{NO}_3^-$  in the PPy prepared from the  $2 \text{ mol L}^{-1}$   $\text{NaNO}_3$  solution is 0.33, similar to that in common PPy( $\text{TsO}^-$ ) films, while that

**Table II** Results of Elemental Analysis of PPy Films (on the Front Side of the Anode) Prepared in pH 3,  $0.1 \text{ mol L}^{-1}$  Pyrrole Aqueous Solutions with Different Concentrations of  $\text{NaNO}_3$  at a Constant Current of  $1 \text{ mA cm}^{-2}$

Electrolyte Concentrations ( $\text{mol L}^{-1}$ )	Mol Ratios				
	C	H	N	$\text{NO}_3^-$	$\text{O}^a$
0.2	4	3.39	1	0.24	0.74
1	4	3.36	1	0.29	0.52
2	4	3.32	1	0.32	0.49
4	4	3.26	1	0.32	0.54

<sup>a</sup> As balance.

in the PPy prepared from the 0.2 mol L<sup>-1</sup> NaNO<sub>3</sub> solution is only 0.24. Another interesting phenomenon is the decrease of the amount of the extra oxygen in PPy with the increase of the electrolyte concentration: 0.74 for the 0.2 mol L<sup>-1</sup> NaNO<sub>3</sub> solution decreased to 0.49 for the 2 mol L<sup>-1</sup> NaNO<sub>3</sub> solution. So, the electropolymerization processes of pyrrole were affected positively by the increase of the electrolyte concentration on the polymerization solutions.

## CONCLUSIONS

The electrolyte concentration is one of the important conditions in the electropolymerization of pyrrole. The doping degree of the counteranions, the conductivity, and tensile strength of the as-prepared PPy films increased with increase of the electrolyte concentration. The NO<sub>3</sub><sup>-</sup> doping degree of 0.24 in the PPy(NO<sub>3</sub><sup>-</sup>) film prepared from the 0.2 mol L<sup>-1</sup> NaNO<sub>3</sub> aqueous solution increased to 0.33 in the film obtained from the 2 mol L<sup>-1</sup> NaNO<sub>3</sub> solution. The conductivity and tensile strength of the as-prepared PPy films increased by ca. 50–70% when the electrolyte concentration changed from 0.2 to 1 mol L<sup>-1</sup>. Further increase of the electrolyte concentration over 1 mol L<sup>-1</sup> has little effect on further improving the quality of PPy. So, 1 mol L<sup>-1</sup> is recommended for the selection of the electrolyte concentration in the aqueous solutions of pyrrole polymerization.

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