Protonic Acid Doping Form in Poly(*N*-methylpyrrole)

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ABSTRACT: The counter-anion doping states of poly(*N*-methylpyrrole) (PNMP) were studied by elemental analysis, mass analysis, cyclic voltammetry, electrochemical quartz crystal microbalance (EQCM) and Vis-NIR spectra measurement. A part of counter anions and H^+ cations left the PNMP film when it was immersed in distilled water, leading to the mass loss of the film, and the pH value drop of the water. The electro-chemical activity and doping level of the polymer in aqueous solution decreased with the increase of the solution pH value. The protonic acid doping form is proposed as one of the doping forms in PNMP, and deprotonation takes place in neutral and basic aqueous solutions.
    KEY WORDS   Poly(*N*-methylpyrrole) / Protonic Acid Doping / Deprotonation / Electrochemical Properties /

Conducting polymers can switch between conducting and insulating state by doping and dedoping.[1-6] Doping is an essential matter in the study of conducting polymers. Two different doping forms have been proposed for conducting polyaromatic compounds, that is, the oxidation doping form and the protonic acid doping form. The difference between them is that the former involves a loss of electron of the conjugated π-system (oxidation) while the latter involves no change in number of electron of the conjugated system. Protonic acid doping form was proposed in the study of polyaniline (PAn).[3] It has been clear that the doping form in PAn is protonic acid doping on nitrogen atom, and the switching of PAn between the conducting state and the insulating state is attributed to protonation in acidic solution and deprotonation in basic solution. But this doping form does not exist in polythiophene.[4]

It has been proposed that both doping forms exist in polypyrrole (PPy). And the existence of protonic acid doping form in PPy has been proved by many evidences, such as the measurement of elemental analysis,[5] FT-IR spectra,[7] *in-situ* VIS-NIR spectra,[5,8] XPS, TGA, high temperature conductivity measurement[9] and the change of pH value of water immersed with the PPy film.[6] This doping form is lost in basic solution and re-obtained in acidic solution. The doping degree of protonic acid in PPy is related to both the doping counter-anions and the pH value of the preparation solution. For example, the doping degree of protonic acid in PPy film increased with such order as: $PPy(TsO^-) < PPy(ClO_4^-) < PPy(NO_3^-)$.[6] Two different protonation structures, β-protonation and *N*-protonation, were considered before[5,7,10]:

β-Protonation   *N*-Protonation
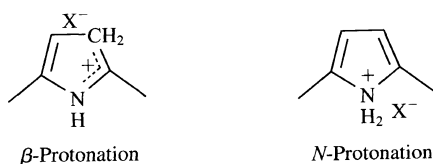
where X^- represents the counter-anion in PPy. In fact,

pK_a is -5.90 for β-protonation and -10 for *N*-protonation. So the possibility of β-protonation will be one thousand times higher than that of *N*-protonation.[11] Hence it is reasonable to consider that the dominant structure of proton acid doping is the β-protonation.

Now the argue is what is the origin of the deprotonation of PPy in a basic solution. One may think the deprotonation of PPy in neutral and basic solutions is not from the protonated structure but from the hydrogen connecting to N of the pyrrole ring[10]:
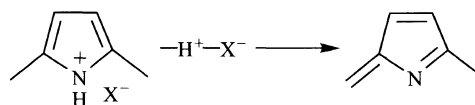
To elucidate this problem, poly(*N*-methylpyrrole) (PNMP) could be a good candidate. It has been found that PNMP is polymerized through the same mechanism as its parent.[12] Methyl group in place of hydrogen atom connecting to N in pyrrole ring will not significantly influence the electron distribution on pyrrole ring. But it makes the deprotonation from N impossible. So, if the deprotonation could be observed in PNMP, it should come from the protonic acid doping structure. Then this could be used to support the existence of the proton acid doping structure of PPy.

In this paper, many evidences show that the protonic acid doping form does exist in PNMP.

EXPERIMENTAL

PNMP films were electrochemically polymerized at 0.80 V *vs.* SCE on a stainless steel plate or an indium–tin oxide (ITO) glass (for optical spectroscopy) electrode in an aqueous solution of 0.1 M *N*-methylpyrrole and 0.2 M $NaNO_3$ or 0.2 M TsONa adjusted to pH 3 by adding corresponding acid. The thickness of the film formed was 10—20 μm for the conductivity measurement, elemental analysis and mass measurement, and it was *ca.* 0.3 μm (60 mC·cm^{-2}) for taking optical absorption spectra.

The total charge consumed during the polymeriza-

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tion was 40 mC on a Au disc with 6 mm diameter for cyclic voltammetry (CV) and EQCM measurement. CV measurement was carried out using an EG & G PAR model 174 A polarographic analyzer and Model 175 Universal Programmer with the Au disc as the working electrode, a Pt plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A potential scan rate of $20 \, \text{mV s}^{-1}$ was used in the CV measurement.

Frequency change of EQCM was measured using ADVANTEST R5361 frequency counter. A 5 M Hz AT-cut quartz crystal with 6 mm diameter gold deposit was used as the working electrode in the EQCM study. VIS-NIR absorption spectra were recorded with Nanometrics Nanospec/10 (VIS) and Nanospec/10 NIR (NIR) Microspectrophotometer.

The conductivity of the films was measured with two probe technique using ADVANTEST R8340 Ultra High Resistance Meter. The pH value of solution was measured using KENT EIL 7045/46 pH Meter.

All potential in this paper referred to SCE.

RESULTS AND DISCUSSION

Chemical Composition of the PNMP Film after Water or Basic Solution Treatment

In order to investigate the stability of the counter-anions in PNMP, elemental analysis was performed for the poly(N-methylpyrrole) toluenesulphonate [PNMP (TsO$^-$)] after immersed in distilled water or 0.2 M TsONa aqueous solution of pH 12 for eight hours. The results are shown in Table I. It is interesting to note that the amount of TsO$^-$ in the polymer decreased after the distilled water treatment, revealing that some TsO$^-$ counter anions have been excluded from the polymer. Since the ion concentration in distilled water is so low that the ion exchange process between the polymer and the distilled water can not take place, the change of doping level must be caused by the de-intercalation of TsO$^-$ from the polymer. The amount of TsO$^-$ in PNMP (TsO$^-$) after immersed in basic solution decreases even more than that after immersed in water. The similar composition change has been observed for PPy(NO$_3^-$) after such treatment.[5]

Mass Change of PNMP Film after Distilled Water Treatment and pH Value Change of the Water

The oxidized PNMP polymer is in electrically neutral state in which the positive charges on the polymer backbone are compensated by the counter-anions. To maintain the electrically neutral state, the expulsion of the counter-anions from the PNMP film in distilled water must accompany with the leaving of cations from the

polymer. This is proved by the following experiments.

A PNMP(TsO$^-$) film of 6.11 mg immersed in 20 ml distilled water for eight hours, its mass and the pH value of the water was measured before and after the treatment. After the treatment, the pH value of the water droped from 5.86 to 3.68, indicating that the leaving of H$^+$ cations from the polymer to water has taken place. The amount of the leaving H$^+$ cations is calculated to be 4.2×10^{-6} mol according to the pH change of the water. At the same time, the mass of the film was weighted to be 5.25 mg after the treatment. The mass of the film lost 0.86 mg. The mass loss of the polymer may be the result of the leaving of TsO$^-$ anions and H$^+$ cations from the polymer. The amount of the leaving TsOH species is calculated to be 5.0×10^{-6} mol according to the mass loss. Because of part mass loss during the transfer process of the film and the error (± 0.06) of pH measurement, both data could be thought in agreement with each other. This verifies that the process during the water treatment is the leaving of TsOH species from the polymer. These results demonstrate that there exists proton acid doping form in PNMP and its deprotonation takes place in distilled water.

Effect of Solution pH Value on the Electrochemical Activity of PNMP

The electrochemical activity of PNMP was investigated by CV and EQCM in the solutions of various pH values.

EQCM is a valuable tool for detecting the slight mass change of the film electrode and it is widely employed in the study of the ion transfer process of PPy.[13,14] The relationship between the mass change (ΔM) and the resonant frequency shift (Δf) of the crystal is described by the Sauerbrey equation[15]

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

where f_0 is the resonant frequency of the unloaded quartz crystal, A is the surface area of the electrode, ρ_q is the density of the quartz crystal ($2.468 \, \text{g} \cdot \text{cm}^{-3}$) and μ_q is the sheer modulus of quartz ($2.947 \times 10^{11} \, \text{dyn cm}^{-2}$). Here, EQCM was used to study the mass change of PNMP during the redox process.

The electrochemical process of PNMP(TsO$^-$) was investigated by CV and EQCM between -0.30 V and $+0.65$ V in aqueous 0.2 M TsONa solution of pH 3, as shown in Figure 1. The electrochemical process shows
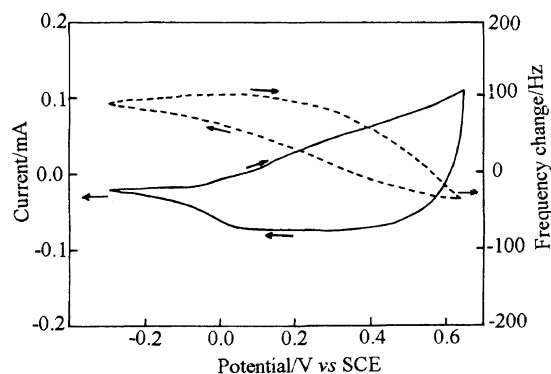
Table I. Results of elemental analysis of PNMP(TsO$^-$)

Sample	C	H	N	S (TsO$^-$)	O (Excess)
a. As-prepared	5.91	5.41	1	0.127	0.98
b. Treatment by distilled water	5.33	5.02	1	0.057	1.07
c. Treatment by 0.2 M TsONa of pH 12	5.48	5.01	1	0.043	1.11

Figure 1. Current (—) and frequency (- - -) responses of PNMP(TsO$^-$) in 0.2 M TsONa solution of pH 3 during a triangular potential scan between -0.30 V and $+0.65$ V.
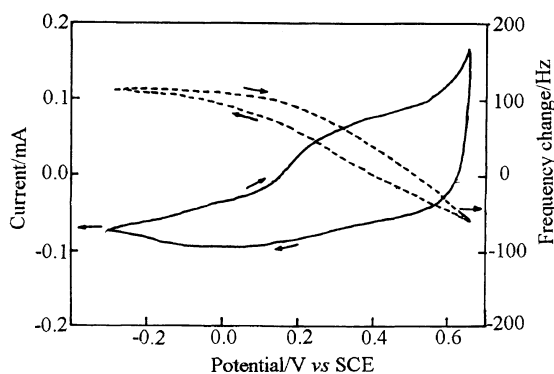
Figure 2. Current (—) and frequency (---) responses of current and frequency responses of PNMP(NO$_3^-$) in 0.2 M NaNO$_3$ solution of pH 3 during a triangular potential scan between −0.30 V and +0.65 V.

Table II. The reduction charge integrated from CV curve and frequency change from EQCM for the PNMP(NO$_3^-$) film of 40 mC during the reduction from +0.65 V to −0.20 V in the solutions of various pH

Solution pH	Reduction charge	Frequency increase
	mC	Hz
3	0.90	175
7	0.75	150
9.4	0.69	140
10.2	0.57	110
11.4	0.41	75

good reversibility of reduction and reoxidation. The reduction charge integrated from the CV curve between 0.65 V and −0.30 V is 0.85 mC. EQCM experiments monitoring the process showed that the crystal frequency kept increasing during the reduction. This reveals that the film mass keeps decreasing during the reduction. Reversibly, the increase of the film mass is observed during the oxidation from −0.30 V to +0.65 V. The frequency increase is 155 Hz during the reduction from +0.65 V to −0.30 V.

When analogous experiments were performed for the PNMP(TsO$^-$) film in neutral 0.2 M TsONa aqueous solution, the CV and EQCM measurement showed similar results to that in the above acidic solution. The reduction charge integrated from the CV curve is 0.75 mC and the frequency increase is 120 Hz during the reduction from +0.65 V to −0.30 V. Compared with the results in acidic solution, both the electrochemical activity and the doping level decrease in neutral solution. These show that the de-intercalation of part TsO$^-$ anions from the polymer takes place in neutral solution, leading to the lose of part electrochemical activity. These prove the existence of protonic acid doping form in PNMP further.

In order to explore the generality of the above observation, analogous studies were performed for PNMP (NO$_3^-$) in 0.2 M NaNO$_3$ aqueous solutions of pH 3, 7, 9.4, 10.2, and 11.4. In the solution of pH 3, good reversibility of the redox process was observed on the cyclic voltammograms and similar tendency of frequency change to that for PNMP(TsO$^-$) was observed by the EQCM measurement during the redox process (see Figure 2). The reduction charge integrated from the CV curve and the frequency increase during the reduction from +0.65 V to −0.30 V were obtained for PNMP(NO$_3^-$) in the solution of various pH value, as shown in Table II. We can find that the reduction charge decreases with the increase of NaNO$_3$ solution pH value. It is 0.90 mC in the solution of pH 3 but decreases to 0.41 mC in the solution of pH 11.4. The electrochemical activity has lost by 54%. EQCM experiments show that the frequency change during the reduction is 175 Hz in the solution of pH 3. It decreases to 75 Hz in the solution of pH 11.3. These reveal that the doping degree decreases by 57% in the pH 11.3 solution. Both data agree with each other very well, indicating that the loss of part electrochemical activity in the basic solution is the result of the decrease of the doping degree of the counter anions in the polymer.
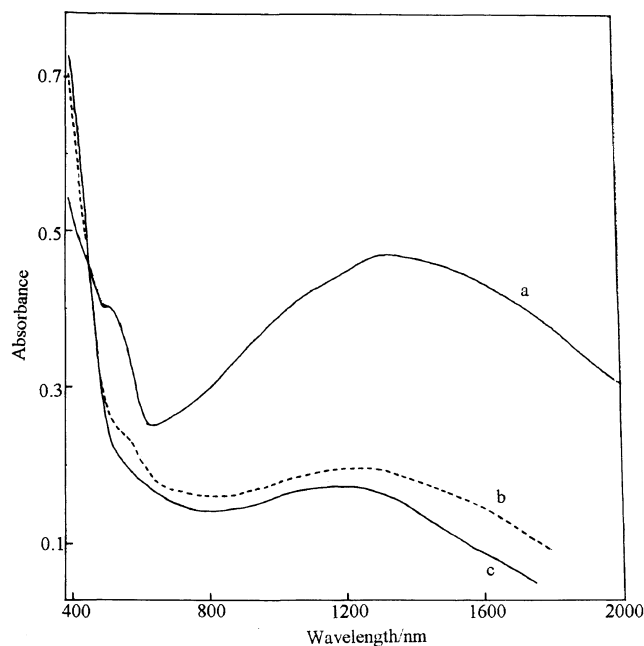

Figure 3. VIS-NIR absorption spectra of PNMP(TsO$^-$). a, as-prepared; b, after immersed in distilled water for two hours; c, after immersed in 1 M NaOH solution for 30 min.

Conductivity and VIS-NIR Spectra after Water or Aqueous Basic Solution Treatment

The conductivity of the as-prepared PNMP(TsO$^-$) film is 10^{-3} S cm^{-1}. It decreased to 10^{-4} S cm^{-1} after immersed in distilled water for eight hours and decreased to 10^{-6} S cm^{-1} after immersed in 1 M NaOH aqueous solution for two hours. The decreasing degree of the conductivity of the PNMP(TsO$^-$) film is similar to that of the PPy(NO$_3^-$) film after the same treatment.[5,6] The decrease of the conductivity of the PNMP(TsO$^-$) film after the distilled water treatment should be the result of the decrease of the doping level due to the deprotonation.

PNMP film showed not only the drop of its conductivity but also the change of its color after distilled water or aqueous basic solution treatment. The color of the as-prepared PNMP(TsO$^-$) film was brown and turned to yellow green after the treatment. VIS-NIR spectra of the PNMP(TsO$^-$) film were recorded before and after the water or 1 M NaOH aqueous solution treatment, as shown in Figure 3. On the VIS-NIR spectra of the as-prepared PNMP(TsO$^-$) film, two absorption peaks are observed at 530 nm and at *ca.* 1300 nm, and the latter peak is much stronger than the former one.
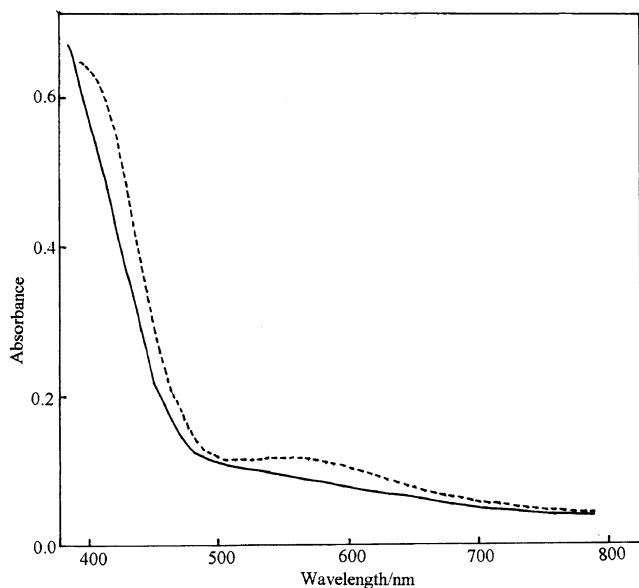
Figure 4. *In-situ* VIS spectra of PNMP electrochemically reduced at −0.20 V in 0.2 M TsONa solution of pH 3 (---) and pH 7 (—).

After the treatment in distilled water, the absorption in NIR region drops greatly. At the same time, the absorption peak at 530 nm decreases a lot but the absorption peak still exists. The absorption peak at 530 nm disappears after the NaOH solution treatment. These indicate that the absorption peak at 530 nm may be related to the protonic acid doping form in PNMP, which will be studied further in the following experiments. Similar absorption peak has been observed between 400 and 600 nm for the PPy film and it disppeared too after the basic solution treatment.[5]

If the above PNMP film treated by distilled water is re-treated by acidic TsONa aqueous solution, the absorption in VIS-NIR region returned to its original intensity. These reveal that the deprotonation of the PNMP film in distilled water reversibly takes place in acidic solution.

In-Situ VIS Spectra of PNMP

The *in-situ* VIS spectra of the reduced PNMP film at −0.20 V were recorded in 0.2 M TsONa aqueous solution of pH 3 and pH 7, as shown in the Figure 4. It is interesting to note that the absorption maxima at 560 nm are observed on the *in-situ* VIS spectra in acidic solution while it is not observed in neutral solution, revealing that the absorption maxima are related to H⁺ cations in the solution. Similar phenomenon has been observed for PPy and the absorption maxima at around 470 nm are proposed to be a characteristic of the protonation of reduced PPy.[8]

The electrochemical oxidation of PNMP(TsO⁻) was investigated by *in-situ* VIS spectra in TsONa aqueous solution of pH 3 from −0.20 V to +0.60 V as shown in Figure 5a. The PNMP(TsO⁻) film was reduced at −0.20 V at first, then it was reoxidized to +0.60 V step by step. With the increase of the potential from −0.20 V to 0.30 V, the absorption maxima at 560 nm become more and more pronounced and shift to 530 nm with the absorbance of 0.32 at 0.3 V.
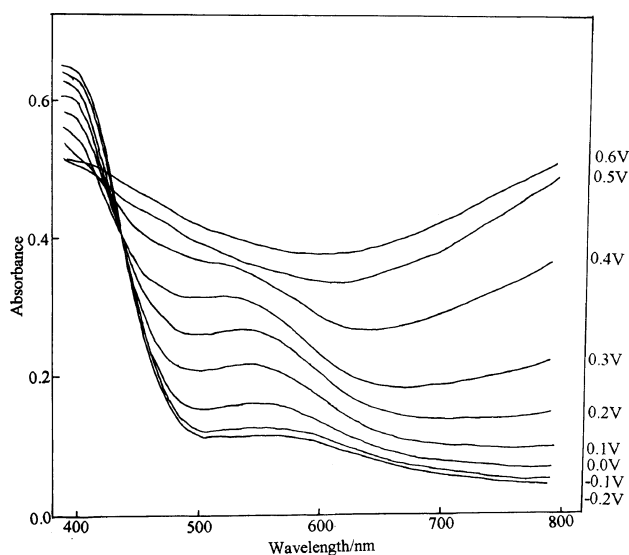
In order to investigate the effect of the solution pH

Figure 5a. *In-situ* VIS absorption spectra of PNMP(TsO⁻) in aqueous 0.2 M TsONa solution of pH 7 during the oxidation from −0.20 V to +0.60 V.
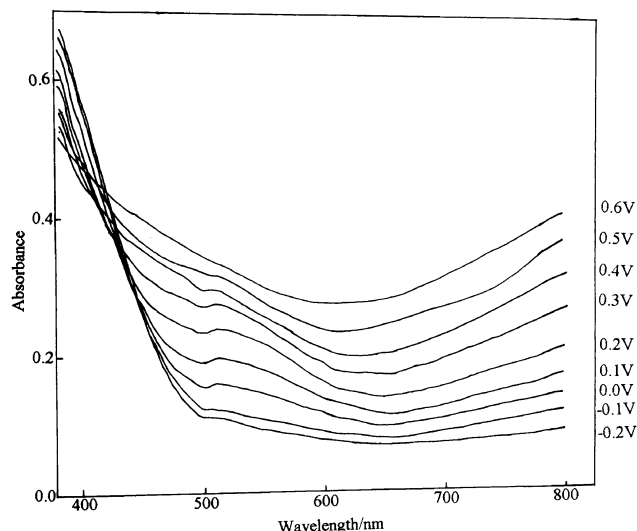

Figure 5b. *In-situ* VIS absorption spectra of PNMP(TsO⁻) in aqueous 0.2 M TsONa solution of pH 3 during the oxidation from −0.20 V to +0.60 V.

value, analogous experiments were performed for the PNMP(TsO⁻) film in neutral 0.2 M TsONa solution, as shown in Figure 5b. The intensity of the absorption is weak than that in the acidic solution at a same potential. At 0.30 V, the absorbance at 530 nm is 0.27, comparing with the absorbance of 0.32 in the acidic solution. From the above results, it is reasonable that the absorption peak between 500 nm and 600 nm is a characteristic of the protonic acid doping form in PNMP.

Morphology of PNMP

The structure change of PNMP immersed in aqueous basic solution should lead to some rearrangement of polymer chain packing in the PNMP surface before and after basic solution treatment. The as-prepared PNMP (NO₃⁻) films showed a granular morphology (see Figure 6a). Upon treatment, the granules become smaller and more compactly packed (see Figure 6b).
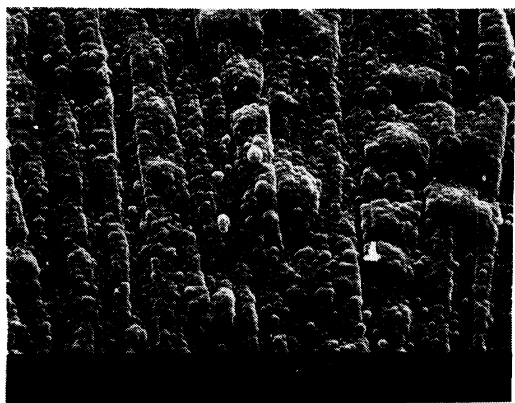
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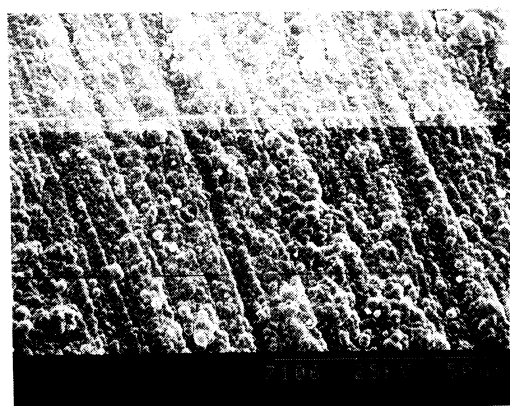
b

Figure 6. Surface electron micrographs of a $PNMP(NO_3^-)$ film. a, as-prepared; b, after 1.0 M NaOH solution treatment.

CONCLUSION

1. After the treatment of distilled water or basic aqueous solution, the amount of the counter-anions

TsO^- in $PNMP(TsO^-)$ film, the mass of the film and the pH value of the water decreased. The leaving of some TsOH species from the film and the existance of the proton acid doping structure of PNMP were proposed.

2. The electrochemical activity of PNMP in solution is related to the pH value of the solution. It decreases with the increasing of the solution pH as the result of deprotonation.

3. The absorption maxima at 560 nm on the *in-situ* VIS spectra of PNMP at -0.20 V increase with increasing potential and shift to 530 nm at 0.3 V. The aborption maxima may be a characteristic of the protonic acid doping form in PNMP.

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