

ELECTROCHEMICAL POLYMERIZATION OF ANILINE IN PHOSPHORIC ACID AND THE PROPERTIES OF POLYANILINE*

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Abstract The behavior of the electrochemical polymerization of aniline in a weak acid, phosphoric acid, is very similar to that in strong acids, *i.e.* its polymerization rate increases quickly with the electrolysis time. The FTIR spectra of polyaniline samples synthesized in phosphoric acid indicate that the counter ion H_2PO_4^- is present in both the oxidized form and the reduced form of polyaniline. The counter ion plays an important role in adjusting the pH value at the electrode surface of polyaniline during the oxidation and reduction processes. As a result, a pair of redox peaks still appear in cyclic voltammograms of polyaniline in a solution of sodium sulfate of pH 5.5 and in a solution of NaH_2PO_4 of pH 7.0, respectively, at low potential scan rate; and the color of polyaniline film also changes with applied potential at pH 7.0. Thus, the pH region for the electrochemical activity and the electrochromism of polyaniline is extended to pH 5.5 for a solution of sodium sulfate and to pH 7.0 for a solution of NaH_2PO_4 . The conductivity of polyaniline is 3.3 S cm^{-1} , depending on the concentration of phosphoric acid used in the stage of polymerization of aniline. The result of elemental analysis of polyaniline is presented here.

Keywords Electrochemical polymerization, Polyaniline, Spectroelectrochemistry, FTIR spectra, Elemental analysis

INTRODUCTION

Polyaniline has been extensively studied since the interconversion of metallic and insulating forms was reported^[1]. This is due to its high conductivity, high redox reversibility, fast change in film color with potential and good stability in air and aqueous solutions. Polyaniline can be prepared by chemical or electrochemical oxidative polymerization of aniline. Regardless of chemical or electrochemical polymerization, strong acids, such as HCl ^[1, 2], HNO_3 ^[3, 4], HClO_4 ^[5, 6], H_2SO_4 ^[7, 8], HBO_4 ^[9, 10] and camphor sulfonic acid^[11, 12] were used to prepare polyaniline. Only few papers reported the chemical oxidative polymerization of aniline in weak acids, such as phosphoric acid^[13, 14], phosphonic acid^[15], 3-pentadecylphenylphosphoric acid^[16], and the electrochemical polymerization of aniline in phosphate buffer solution^[17] and in aqueous acetate buffer solution^[18]. This is due to the fact that polyaniline prepared in strong acids has a high conductivity and good electrochemical properties. And the polymerization rate of aniline in the strong acids is much faster than that in the weak acid. Especially for the electrochemical polymerization, polyaniline film hardly grows during the electrolysis of aniline in weak acid. It is well known that the electrochemical activity of polyaniline decreases with increasing pH value, and polyaniline has a little electrochemical activity at $\text{pH} \geq 4$. This is unfavorable for its use in rechargeable batteries and electrocatalysis. So from the point of view of electrochemical applications, the applicable pH region for the electrochemical activity of polyaniline must be extended to higher pH values. Among various factors affecting the properties of polyaniline, the dopant ion, *i.e.* counter ion, is very important. This is because the properties of polyaniline, such as conductivity^[19, 20], morphology^[21, 22], processability^[11, 23] and electroactivity^[24, 25] are markedly affected by dopant ions. However, the dopant anions of the strong acids mentioned above are unable to

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improve the pH dependence of polyaniline, since they have no buffer capacity. In dopant acids, polyatomic acids can play a role in adjusting the pH value. The electrochemical polymerization of aniline in some polyatomic organic acids was studied in our laboratory. The results indicate that the polyaniline film is quite difficult to grow as the electrolysis proceeds, the conductivity and electrochemical activity of polyaniline prepared in polyatomic acids are very low. This is because all polyatomic acids are mostly weak acids, and the protonation of aniline in a weak acid is very weak.

Phosphoric acid is a weak acid. It appears to be not a good dopant acid for polyaniline since polyaniline synthesized in weak acids has low conductivity and poor electrochemical activity. Especially, the film growth is very slow during the electrochemical polymerization of aniline in weak acids. This is the reason why phosphoric acid has not been receiving attention in the preparation of polyaniline. However, polyaniline prepared by chemical oxidative polymerization in the presence of phosphoric acid has a relatively high conductivity of 40–50 S cm⁻¹[13, 14]. Its conductivity is even higher than that of polyaniline synthesized in strong acids. Although phosphoric acid is ionizable in water, which is favorable for the adjusting the pH value, there is no report on the electrochemical polymerization of aniline in the aqueous solution of phosphoric acid and the electrochemical properties of the polymer. In this work, we attempted to study the electrochemical polymerization of aniline in phosphoric acid and to see whether the pH dependence of polyaniline could be affected by the counter ions.

EXPERIMENTAL

The chemicals used were all of reagent grade. The concentration of phosphoric acid was 98%. Aniline was distilled before use. Doubly distilled water was used to prepare solutions. The pH value of the NaSO₄ solution was adjusted by sulfuric acid. The pH of NaH₂PO₄ solution was adjusted by phosphoric acid or sodium hydroxide solution. The electrolysis cell consisted of two platinum foil electrodes and a reference electrode. The area of the working electrode was 4 × 4 mm². All potentials given here are referred to the saturated calomel electrode (SCE), except in the experiment of the *in situ* visible spectra.

A HPD-1A potentiostat-galvanostat and a PAR Model 173 potentiostat-galvanostat with a Model 179 digital coulometer were used for the electrochemical measurements. The cyclic voltammograms were recorded on a YEW 3036 X-Y recorder. The *in situ* visible spectra of polyaniline films were measured on an UV-2501 PC UV-vis recording spectrophotometer at different potentials. The cell for the spectroscopic experiments consisted of a polyaniline/ITO (indium-tin oxidized) working electrode, a net form platinum counter electrode and an Ag/AgCl reference electrode (with saturated KCl solution). Polyaniline film was polymerized electrochemically on an ITO conducting glass prior to the spectroscopic experiments. The measurements of the spectra were conducted at an interval of 1.5 min between two measurements after the potential was changed. The corresponding measured solution and an ITO conducting glass without the polymer were transferred into a reference cell of the spectrophotometer.

Polyaniline samples used for the following experiments were prepared electrochemically at 0.75 V, and then washed with phosphoric acid solution of pH 2. Polyaniline samples for the determination of conductivity were dried at 90°C for 24 h in air, which was measured on a pellet with a diameter of 13 mm and thickness of 0.7–0.8 mm, using a four-probe technique. FTIR spectra of the oxidized form and reduced form of polyaniline were measured on KBr pellets using a Nicolet 740 FTIR instrument. The oxidized form of polyaniline was prepared by electrolysis at a constant potential of 0.75 V, and the reduced form of polyaniline was obtained by the electrochemical reduction of the oxidized polyaniline in the HCl solution of pH 2 at -0.30 V for 40 min, and then washed thoroughly using doubly distilled water to remove any phosphoric acid adsorbed on polyaniline as completely as possible. The reduced form of polyaniline is not stable at ambient conditions and undergoes oxidation if there are traces of residual phosphoric acid on the surface of polyaniline. The oxidized and reduced forms of polyaniline samples for determination of FTIR spectra were dried first at 95°C for 16 h, and then dried again at 130 and 150°C for 7 h, respectively. A Carlo Erba elemental analyzer Model 1106 (Italy) was used for elemental analysis of polyaniline samples.

As mentioned above, polyaniline samples used for the following experiments were prepared

electrochemically at a constant potential of 0.75 V, but cyclic voltammetry was also used for the preparation of polyaniline in this work. This is because cyclic voltammetry can give much information on the electrochemical polymerization of a monomer, such as the polymerization potential of the monomer, the process of the current peak formation and the changes in the polymerization rate and polymer film growth with respect to time. Here the scan potential range was set between -0.20 and 1.20 V, and the scan rate was controlled at 60 mVs^{-1} for the electrochemical polymerization of aniline. In comparison with the constant potential method, the disadvantage of cyclic voltammetry is that its current efficiency for the electrochemical polymerization is much lower than that of the constant potential method. This is due to the fact that a portion of charge was consumed in the electro-reduction of polyaniline film during the reverse scan. The current efficiency was nearly 100% for the electrochemical polymerization of aniline at 0.75 V.

RESULTS AND DISCUSSION

Electrochemical Polymerization of Aniline in Phosphoric Acid

The cyclic voltammograms of polyaniline film growth during the electrolysis of aniline were carried out in a solution containing 0.2 mol dm^{-3} aniline and 1.2, 3.4 and 6.8 mol dm^{-3} phosphoric acid, respectively. PAn-P here is denoted as polyaniline prepared in phosphoric acid. One feature that the cyclic voltammograms in three plots have in common is that both the oxidation current and the reduction current increase with increasing number of potential cycles. This result is very similar to that of the electrochemical polymerization of aniline in strong acids^[26, 27], which is caused by the autocatalytic polymerization of aniline^[28, 29]. So, the electrochemical polymerization of aniline in phosphoric acid is also an autocatalytic polymerization. As a result, polyaniline film in this case grows quickly during the polymerization process.

For the sake of simplicity, only a cyclic voltammogram of polyaniline film growth in $3.4 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ solution is shown in Fig. 1. The anodic peak potential of aniline is 1.05, 1.10 and 1.20 V, in 1.2, 3.4 and $6.8 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$, respectively. Therefore, the polymerization potential of aniline increases with increasing concentration of phosphoric acid, which is caused by protonation of aniline since a protonated molecule is oxidized at a higher positive potential than an unprotonated one^[30]. This phenomenon is analogous to that of the electrochemical polymerization of aniline in strong acids^[25]. The cyclic voltammograms show that the oxidation current and reduction current at the same cycle in three plots increase with increasing concentration of phosphoric acid.

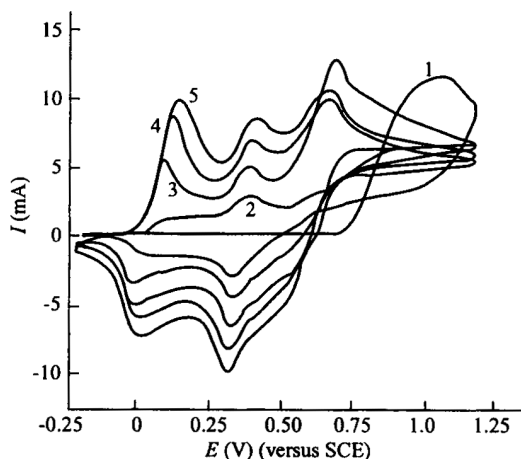


Fig. 1 Electrochemical polymerization of aniline in $3.4 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ solution
Curves 1–5 correspond to the number of cycles; Scan rate is 60 mVs^{-1} .

In general, polyaniline in a solution without aniline is easily degraded when the potential is over 0.8 V, depending on the pH value of the solution. This is caused by the overoxidation and hydrolysis of polyaniline.

However, polyaniline is more stable towards hydrolysis in an aniline-containing solution^[31]. We also found that polyaniline in the presence of aniline can not be overoxidized when the scan potential is set between -0.20 and 1.10 V^[25]. It is evident that the current increases with increasing number of potential cycles (Fig. 1), and the cyclic voltammogram of polyaniline prepared in this manner is the same as that of material synthesized at 0.75 V, which will be shown below.

The above results demonstrate that even though phosphoric acid is a weak acid, the behavior of the electrochemical polymerization of aniline in phosphoric acid is very similar to that of the electrochemical polymerization of aniline in strong acids. Therefore, polyaniline is readily prepared in phosphoric acid using the electrochemical method.

FTIR Spectra of Polyaniline

The FTIR spectrum of polyaniline prepared chemically in phosphonic acid has been reported^[15], but no vibrations bands of the $P=O$ bond or phosphonate anions were detected. It is assumed that their absorption peaks are masked by the more intense absorption peaks of the polyaniline skeleton. The IR spectrum of polyaniline prepared chemically in 3-pentadecylphenyl phosphoric acid has been reported^[16], in which no $P=O$ stretching vibrations appear. It is also presumed that its absorption peak is superimposed on the phenyl ring stretching vibration of polyaniline^[16].

The IR spectrum of polyaniline synthesized chemically in phosphoric acid has not been reported. We know that the dopant anion is very important for conducting polymers, and can be detected in the IR spectrum, such as NO_3^- , BF_4^- and SO_4^{2-} doped in polyaniline^[4]. According to the above reports, whether phosphoric acid could be doped into polyaniline or not remains an open question, and whether the dopant anion is PO_4^{3-} or $H_2PO_4^-$ ions remains to be established. Thus, the FTIR spectra of polyaniline, Na_3PO_4 and NaH_2PO_4 were measured here, respectively. The main absorption peaks of Na_3PO_4 should appear at $1443(s)$ and $1041(s)$ cm^{-1} , while those of NaH_2PO_4 are at $1295(s)$, and as a strong broad band with split peaks at 1168 , 1055 , 985 and 929 cm^{-1} .

The FTIR spectra of the reduced form and the oxidized form of PAN-P are presented in Fig. 2, respectively. Here the oxidized form of PAN-P was prepared in 6.8 $mol\ dm^{-3}$ phosphoric acid, and the reduced form of PAN-P was prepared in 3.2 $mol\ dm^{-3}$ phosphoric acid. The peak at 3436 cm^{-1} on spectrum (a) (oxidized form) in Fig. 2 is attributed to $O-H$ stretching vibrations, and a small shoulder peak at 3203 cm^{-1} is assigned to $N-H$ stretching vibrations. Two peaks at 1598 and 1506 cm^{-1} are attributed to stretching vibrations of $C=C$ in aromatic rings. The peaks at 1295 and 1147 cm^{-1} are attributed to $P=O$ in $H_2PO_4^-$ ions based on the IR spectrum of NaH_2PO_4 . The peak at 823 cm^{-1} is assigned to out of plane $C-H$ bending vibrations of aromatic rings.

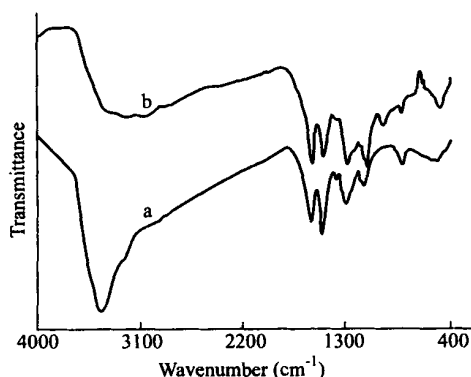


Fig. 2 FTIR spectra of PAN-P
a) Reduced form; b) Oxidized form

In fact, the sample of the oxidized form of PAN-P has also been heated at $150^{\circ}C$ for 7 h just as the sample of the reduced form, but the adsorption bands of water seriously interfered with the spectrum of the oxidized form.

Therefore, the sample of the oxidized form was heated continuously at 170°C for 7 h, and then its spectrum was immediately measured (spectrum b). A broad peak at 3204 cm^{-1} is attributed to N–H stretching vibrations. The peaks at 1591 and 1485 cm^{-1} are attributed to stretching vibrations of C=C in aromatic rings. The peaks at 1288, 1126 and 978 cm^{-1} are assigned to P=O in H_2PO_4^- . The peak at 830 cm^{-1} is due to out-of-plane bending vibration of C–H.

The results obtained from FTIR spectra prove that H_2PO_4^- anions are present in PAN-P, *i.e.* the dopant ion in PAN-P is H_2PO_4^- and not PO_4^{3-} , because the first dissociation constant of H_3PO_4 is much greater than the third one. Water in the oxidized form of PAN-P is more difficult to remove than that in the reduced form of PAN-P and in polyaniline (PAN) prepared in strong acids, even though PAN samples for the determination of IR spectra were dried at a temperature lower than 90°C in air^[4]. The former difference is caused by the doped amount of H_2PO_4^- . The latter difference arises from the kind of dopant anion, since H_2PO_4^- anions are doped into PAN-P, and -OH bonds are included in phosphoric acid^[32].

Effect of pH on Cyclic Voltammograms of PAN-P

All polyaniline films used in this experiment were prepared electrochemically in different concentrations of phosphoric acid at 0.75 V. Figure 3 shows the cyclic voltammograms of PAN-P in 0.2 mol dm^{-3} NaH_2PO_4 solution at different pH values. The scan rate was controlled at 60 mVs^{-1} . PAN-P film used here was prepared in a solution containing 0.2 mol dm^{-3} aniline and 6.8 mol dm^{-3} phosphoric acid. From Fig. 3 we can see that there are two anodic peaks and two cathodic peaks on curve 1 (pH 1.0), curve 2 (pH 2.0) and curve 3 (pH 3.0), respectively. The potentials of the oxidation peak and reduction peak at higher potentials shift towards the negative direction, and the potential of the anodic peak at lower potentials shift towards the positive direction, as the pH value increases from 1.0 to 3.0. The potential of the cathodic peak at lower potentials changes slightly with the pH value. This pH dependence is similar to that of PAN prepared in strong acids^[33, 34]. There is only a pair of redox peaks on curve 4 (pH 4.0), but PAN-P still has a higher electrochemical activity based on the area under curve 4.

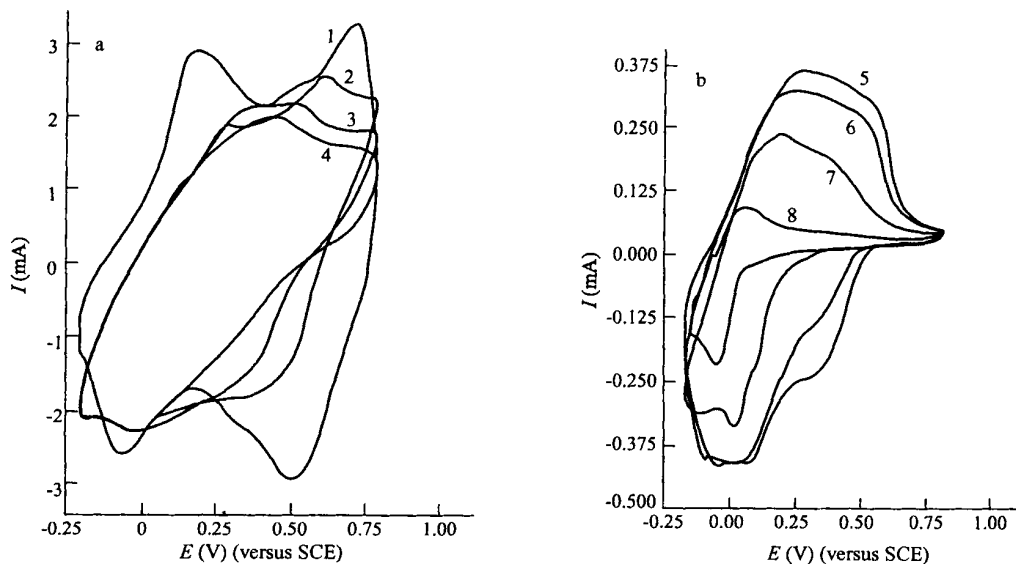


Fig. 3 Effect of pH on the cyclic voltammograms of PAN-P in 0.2 mol dm^{-3} NaH_2PO_4 solution. PAN-P was prepared in 6.8 mol dm^{-3} phosphoric acid.

Scan rate is 60 mVs^{-1} , curves: (1) pH 1.0, (2) pH 2.0, (3) pH 3.0 and (4) pH 4.0

Scan rate is 6 mVs^{-1} , curves: (5) pH 4.0, (6) pH 5.0, (7) pH 6.0 and (8) pH 7.0

Curves 5, 6, 7 and 8 in Fig. 3 show the cyclic voltammograms of PAN-P at pH 4.0, 5.0, 6.0 and 7.0, respectively. The scan rate was set at 6 mVs^{-1} . There are two pairs of redox peaks on curves 5–7. Comparison of

curve 4 and curve 5 shows that only a pair of redox peaks appears on curve 4; however, there are two pairs of redox peaks on curve 5 at the same pH value. This discrepancy is caused by the different potential scan rates. Essentially, this is caused by the low charge transfer of polyaniline at $\text{pH} \geq 4$. The occurrence of redox peaks indicates that the electrode reaction of PAN-P is controlled by mass-transfer. The above result indicates that the electrode reaction of PAN-P in the NaH_2PO_4 solution of pH 7.0 is controlled by mass transfer at a potential scan rate of 6 mVs^{-1} . Thus, PAN-P in NaH_2PO_4 solution of pH 7.0 is still electroactive. This is because the dopant anion in PAN-P is the H_2PO_4^- ion, which has been proved by FTIR spectra. Even in the reduced form, a certain amount of H_2PO_4^- ions is still present in polyaniline. H_2PO_4^- is ionizable in aqueous solution:



The reaction shifts to the right when the pH of the solution increases. The proton generated in reaction (1) plays a role in adjusting the pH value at the electrode surface, which is favorable for the redox of polyaniline because the protons take part in the redox of polyaniline. This is the reason why a pair of redox peaks is still present in the cyclic voltammogram of PAN-P in NaH_2PO_4 solution of pH 7.0 at a scan rate of 6 mVs^{-1} . Another cause is that NaH_2PO_4 solution has a large buffer capacity, which also plays an important role in adjusting the pH value according to Eq. (1). And therefore the pH region for the electrochemical activity of PAN-P is extended.

Figure 4 shows the cyclic voltammograms of PAN-P in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of different pH values. The scan rate was set at 60 mVs^{-1} . The shift of both anodic peak and cathodic peak with pH value in Fig. 4 is analogous to that shown in Fig. 3 in the pH range of 1 to 4, but the electrochemical activity at pH 4.0 (curve 4) in Fig. 4 is much smaller than that on curve 4 in Fig. 3. This is due to the fact that the buffer capacity of Na_2SO_4 solution is much smaller than that of NaH_2PO_4 solution. Curves 5, 6 and 7 in Fig. 4 show the cyclic voltammograms of PAN-P in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at pH 4.0, 5.0 and 5.5, respectively. The scan rate was set at 6 mVs^{-1} . There are two anodic peaks and a cathodic peak on curve 5. This is different from curve 4 because of the different potential scan rates used. A small anodic peak appears on curve 7 (pH 5.5) in Fig. 4, and a cathodic peak almost disappears on curve 7 in Fig. 4. When $\text{pH} > 5.5$, there is neither oxidation peak nor reduction peak in the cyclic voltammogram of PAN-P in sodium sulfate solution at a potential scan rate of 6 mVs^{-1} . This is much different from the situation in Fig. 3, in which a pair of redox peaks also occurs in the cyclic voltammograms. This further indicates that the buffer capacity of solution plays an important role in the electrochemical activity of polyaniline.

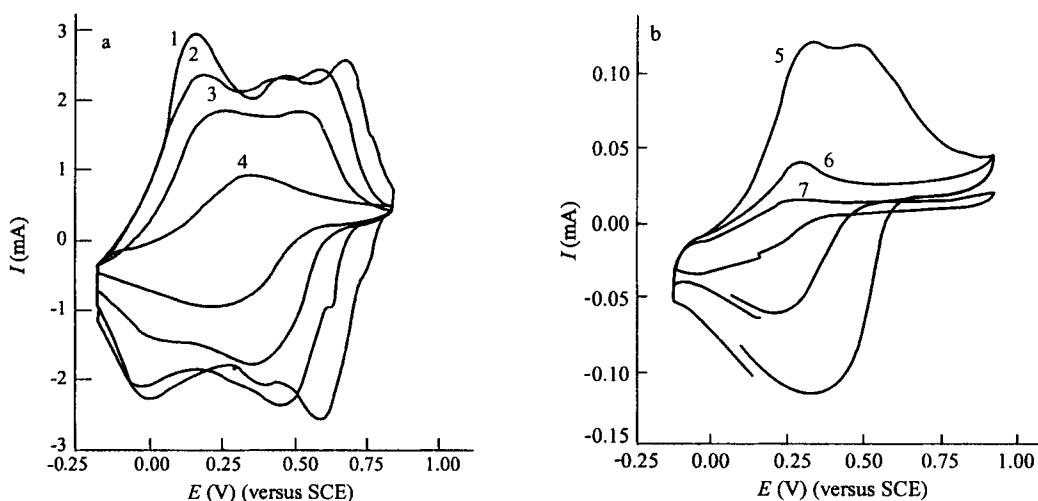


Fig. 4 Effect of pH on the cyclic voltammograms of PAN-P in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution, PAN-P was prepared in 6.8 mol dm^{-3} phosphoric acid

a) Scan rate is 60 mVs^{-1} , curves: (1) pH 1.0, (2) pH 2.0, (3) pH 3.0 and (4) pH 4.0

b) Scan rate is 6 mVs^{-1} , curves: (5) pH 4.0, (6) pH 5.0 and (7) pH 5.5

To interpret further the effect of the buffer capacity of the NaH_2PO_4 on the electrochemical activity of PAN-P, a separate experiment for PAN-P in phosphoric acid solution of $10^{-5} \text{ mol dm}^{-3}$ (pH 4.96) and $10^{-6} \text{ mol dm}^{-3}$ (pH 5.88) was performed at a scan potential range of -0.20 to 0.75 V , and at a scan rate of 6 mVs^{-1} . The results show that two pairs of redox peaks appear in the cyclic voltammogram of PAN-P at pH 4.96, but only one reduction peak at 0.29 V appears in the cyclic voltammogram of PAN-P at pH 5.88. The latter is different from that of curve 7 (pH 6.0) in Fig. 3. According to the area under the I - E curve, the electrochemical activity of PAN-P is much smaller at pH 5.88 than that at pH 4.96, *i.e.*, the electrochemical activity of PAN-P in phosphoric acid solution decreases dramatically from pH 4.96 to pH 5.88. This is also different from that obtained in NaH_2PO_4 solution. This is due to the fact that the buffer capacity of the phosphoric acid solution at such very low concentration is lower than that of $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ solution. Another experimental phenomenon was observed in phosphoric acid solution, that is the reduction current of PAN-P decreases monotonously from potential 0.00 to -0.20 V on the cyclic voltammograms, indicating the degeneration of electrochemical activity of PAN-P, which is also different from those of curves 6 and 7 in Fig. 3.

The suitable pH region for the electrochemical activity of PAN-P prepared in $3.4 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ is the same as that of PAN-P prepared in $6.8 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$. So their cyclic voltammograms are not reported separately here. But the suitable pH region for the electrochemical activity of PAN-P prepared in $1.2 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ is smaller than that of PAN-P prepared in 3.4 mol dm^{-3} . Evidence is that only one cathodic peak appears in the cyclic voltammograms of PAN-P in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 4.0 at a scan rate of 60 mVs^{-1} , but no anodic peak appears.

Effect of pH on Cyclic Voltammograms of PAN

Though the electrochemical properties of polyaniline prepared in strong acids have been reported, it is still necessary to compare the pH dependence of PAN-P with that apparent from the cyclic voltammogram of polyaniline (PAN) prepared electrochemically at 0.75 V in a solution consisting of 0.2 mol dm^{-3} aniline and 0.6 mol dm^{-3} sulfuric acid. Curves 1 and 2 in Fig. 5 show the cyclic voltammograms of PAN in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution at pH 4.0, and pH 5.0, respectively. The scan rate was set at 6 mVs^{-1} . It can be seen that there are one anodic peak and one cathodic peak on curve 1, but only a cathodic peak on curve 2. This is different from that of PAN-P in the same solution at pH 4.0 and pH 5.0, respectively, in which there are still two anodic peaks and a cathodic peak on curve 5 in Fig. 4 (pH 4.0) and a pair of redox peaks on curve 6 in Fig. 4 (pH 5.0). The electrochemical activity of PAN was lost completely in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution at pH > 5.0 at a scan rate of 6 mVs^{-1} .

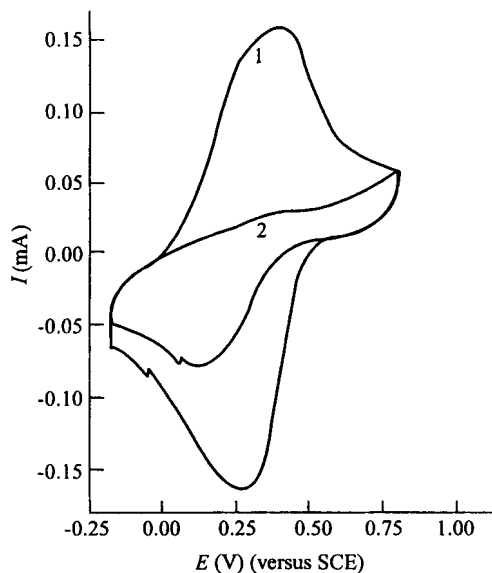


Fig. 5 Effect of pH on the cyclic voltammograms of PAN in $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution
Scan rate is 6 mVs^{-1} ; Curves: (1) pH 4.0 and (2) pH 5.0

The pH dependence of PAn in $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ solution was studied using cyclic voltammetry between -0.2 and 0.8 V at a scan rate of 6 mVs^{-1} . The result shows that there is neither an oxidation peak nor a cathodic peak in the cyclic voltammograms (omitted here) at $\text{pH} \geq 5.5$. This is different from that of PAn-P, in which a pair of redox peaks still appears in the cyclic voltammogram at $\text{pH} 7.0$ (curve 8 in Fig. 3). This means that PAn in $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ solution of $\text{pH} \geq 5.5$ has completely lost its electrochemical activity at a scan rate of 6 mVs^{-1} . The above results prove that the applicable pH region for the electrochemical activity of PAn-P is wider than that of PAn, because the dopant anion in PAn-P is H_2PO_4^- ion.

In situ Visible Spectra of PAn-P and PAn Films

The color of PAn-P film can be changed quickly between yellow and blue with applied potential. In order to determine the suitable pH region and the applied potential region of color change of PAn-P film, the *in situ* visible spectra of PAn-P film in $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ solution at different pH were measured at $-0.30, 0.10, 0.20, 0.30, 0.40, 0.50$ and 0.60 V , respectively. Figures 6(a), (b) and (c) show the visible spectra of PAn-P film in NaH_2PO_4 solution at pH 3.0, 4.0 and 6.0, respectively. An isosbestic point at 368 nm appears in Fig. 6(a) and (b), respectively. However, this isosbestic point disappears in Fig. 6(c). The absorption peak at about 360 nm is due to the $\pi-\pi^*$ transition of benzenoid rings in polyaniline^[35]. Curves 3 to 7 in Fig. 6(a) and curves 4 to 7 in Fig. 6(b) intersect approximately at a common point (441 nm). The wavelength of this isosbestic point is the same as that of polyaniline in $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ solution at $\text{pH} 4.5$ ^[36]. However, curves 1 and 2 in Fig. 6(a) and curves 1 to 3 in Fig. 6(b) do not intersect at a common point. Because polyaniline at -0.30 V (curve 1) and 0.10 V (curve 2) was in reduced form, which leads to a very low absorbance. This phenomenon is similar to that of polyaniline in sodium nitrate solution of $\text{pH} 1.15$ ^[37]. An isosbestic point is characteristic of a system consisting of two chromophores, which are interconvertible. This indicates that PAn-P film has two chromophores in solutions of pH 3.0 and pH 4.0. As the potential moves from -0.30 V (curve 1) to 0.60 V (curve 7), PAn-P is oxidized.

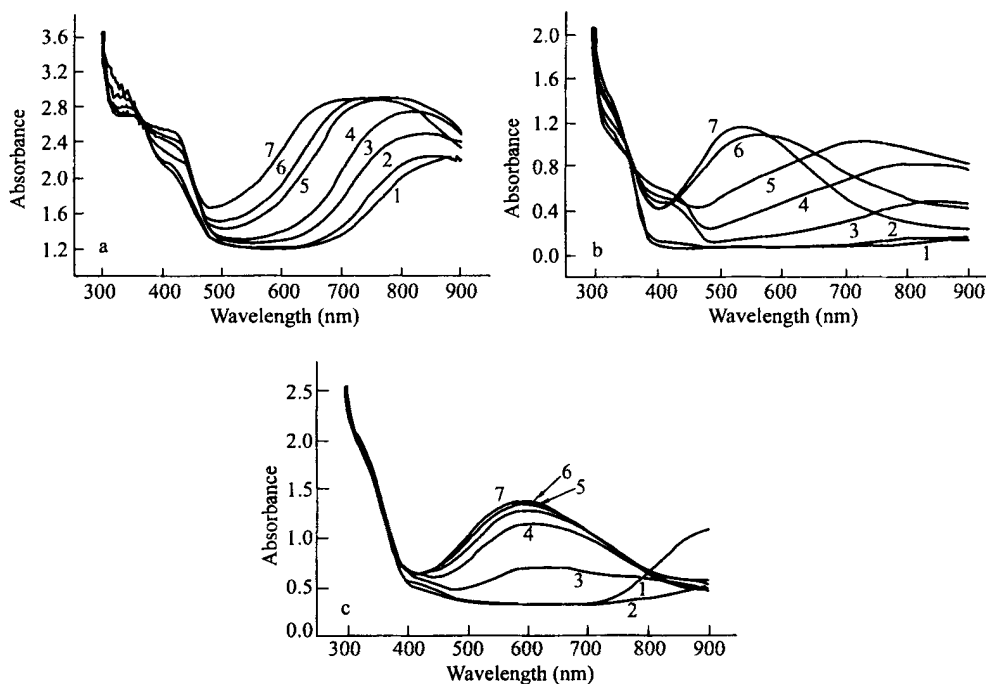


Fig. 6 *In situ* spectra of PAn-P in $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ solutions of different pH values at various potentials (versus Ag/AgCl)

- a) At pH 3.0, curves: (1) -0.30 V , (2) 0.10 V , (3) 0.20 V , (4) 0.30 V , (5) 0.40 V , (6) 0.50 V and (7) 0.60 V
 b) At pH 4.0, curves: (1) -0.30 V , (2) 0.10 V , (3) 0.20 V , (4) 0.30 V , (5) 0.40 V , (6) 0.50 V and (7) 0.60 V
 c) At pH 6.0, curves: (1) -0.30 V , (2) 0.10 V , (3) 0.20 V , (4) 0.30 V , (5) 0.40 V , (6) 0.50 V and (7) 0.60 V

As a result, an absorption peak of PAn-P shifts from 414 to 430 nm and another one shifts from 880 to 670 nm in Fig. 6(a) and from 880 to 530 nm in Fig. 6(b), respectively. In this case, the color of PAn-P film is changed from yellow to deep blue at pH 3.0 and from yellow to near violet at pH 4.0. When the potential of PAn-P in solution at pH 3.0 reaches 0.70 V, its color begins to turn violet. Thus, the potential region for the change of PAn-P film color at pH 3.0 is greater than that at pH 4.0. The change in color with potential is very sharp in the solutions of pH 3.0 and 4.0. The absorption peak at 670 nm is attributed to the π - π^* transition of quinoid rings on polyaniline chain^[35].

There is no absorption peak on curves 1 and 2 in Fig. 6(b). This means that PAn-P in the solution with pH 4.0 can be reduced to leucoemeraldine at -0.30 and 0.10 V at the given time. This is because the electrochemical activity of PAn-P at pH 4.0 is lower than that at pH 3.0. When the reduction time is prolonged, the absorbance near 800 nm on curve 1 in Fig. 6(a) will be dropped, since PAn-P in this case has a higher capacity, *i.e.* a higher activity, which needs a longer time to be completely reduced at -0.30 V.

In the solution of pH 6.0, the peak at about 410 nm almost disappears on curves 1 and 2 in Fig. 6(c), in which PAn-P is in the reduced form. In fact, all curves almost overlap with each other at wavelengths less than 380 nm, independent of potential. So no isosbestic point appears, *i.e.*, PAn-P in this case has only one chromophore. When the potential was set at 0.20 V a broad band occurs at about 850 nm on curve 3. The color of the film is dark blue in this case. As the potential is moved from 0.20 to 0.60 V (curve 7), the absorption peak shifts to 575 nm, at which the color of the film is violet. It is clear that the potential range for the change of film color is narrower than that in the solution of pH 4.0 because there is only one chromophore and a small change in wavelength with potential. That is to say the change in film color is mainly attributed to the change in absorbance. It is clear that a significant increase of absorbance occurs in the vicinity of 800 nm on curve 1 in Fig. 6(c). This is caused by the short reduction time at -0.30 V at the beginning of experiment. Since the electrochemical reaction rate of PAn-P at pH 6.0 is very slow, the time needed to reach the leucoemeraldine form should be prolonged.

The change in color of PAn-P film in NaH₂PO₄ solution at pH 7.0 with potential was also measured, but the extent of change in color is even smaller than that at pH 6.0. The result of the spectroelectrochemical experiments shows that the change in visible spectra of PAn-P film with potential is consistent with the cyclic voltammograms, in which a pair of redox peaks appear in 0.2 mol dm⁻³ NaH₂PO₄ solution of pH 7.0 at a scan rate of 6 mVs⁻¹. This means that the change in color with potential and the redox peaks in the cyclic voltammograms are sensitive indicators of the electrochemical activity of polyaniline because both of them are related to the concentration of proton in the solution.

The *in situ* spectra of PAn film in 0.2 mol dm⁻³ NaH₂PO₄ solution were measured at different potentials (the Figures are omitted here). The results show that the change in the visible spectra of PAn film at pH 4.0 is similar to that of PAn-P film at pH 5.0. This indicates that the pH region for changing the color of PAn film is smaller than that of PAn-P film. The *in situ* visible spectra of PAn film in 0.4 mol dm⁻³ Na₂SO₄ solution at different pH were also determined at the above potential region. The results show that the color of PAn film hardly changes with applied potential at pH > 5.5.

The *in situ* spectroelectrochemical experiments indicate that the color of PAn-P film can change with potential in NaH₂PO₄ solution at pH 7.0.

Elemental Analysis

The results from elemental analysis of PAn-P prepared in different concentrations of phosphoric acid are listed in Table 1.

Table 1. Elemental analysis of PAn-P prepared in different concentrations of phosphoric acid			
Concentration of acid (mol dm ⁻³)	C (%)	N (%)	H (%)
1.2	54.71	10.20	4.40
3.4	50.98	9.65	4.45
6.8	52.63	10.18	4.06

Since PAn-P contains both oxygen and phosphorous, the content of P could not be determined separately. Table 1 shows that the contents of C, N and H in three samples are close to those of PAN prepared in strong acids^[34, 38, 39]. The content of carbon in PAn-P synthesized in $1.2 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ is the largest among the three samples, but the difference for the contents of N and H in the three samples is small. The presence of oxygen in polyaniline has been detected by elemental analysis^[34, 38, 39] and XPS^[40], which may be attributed to oxygen adsorbed strongly on polyaniline.

Conductivity

The conductivity of PAn-P prepared electrochemically in 1.2, 3.4 and 6.8 mol dm^{-3} phosphoric acid is 1.3, 2.3 and 3.3 S cm^{-1} , respectively. The conductivity of PAn-P prepared in $6.8 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ solution is the largest among the three samples, which is very close to that of polyaniline prepared electrochemically in strong acids in our laboratory^[4]. In general, the conductivity of polyaniline is related to the concentration of acid used in the stage of polymerization of aniline. So the above results are to be expected. Additionally, the conductivity of polyaniline is also affected by water content. It is suggested that the adsorbed water greatly decreases the interparticle resistance between metallic islands^[41], and the conduction mechanism of polyaniline can be accounted for in terms of electron hopping between localized states, with the assistance of proton transfer, for which the presence of water plays an essential role^[42]. The result from FTIR spectra shows that water is rather difficult to remove from PAn-P prepared in H_3PO_4 solution, a fact which was caused by the dopant anion of H_2PO_4^- as mentioned above, *i.e.* —OH bonds play a role in enhancing the conductivity as water absorbed in PAN. This is one of reasons for the high conductivity of PAn-P prepared in H_3PO_4 solution.

The conductivity of PAn-P presented here is lower than that of polyaniline prepared by chemical oxidative polymerization in the presence of phosphoric acid, for which the conductivity is $50\text{--}40 \text{ S cm}^{-1}$ ^[13, 14]. A possible reason for this difference is due to the concentration of phosphoric acid used for washing polyaniline and the concentration of aniline used for preparing the polymer. In Refs.[13] and [14] $1 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ was used to wash polyaniline. Such a high concentration of H_3PO_4 can completely prevent the deprotonation of polyaniline, but H_3PO_4 remaining in polyaniline will contribute to its conductivity.

CONCLUSION

Though phosphoric acid is a weak acid, the behavior of the electrochemical polymerization of aniline in phosphoric acid is very similar to that in strong acids. The applicable pH region for the electrochemical activity and electrochromism of PAn-P is extended. Thus, the pH dependence of PAn-P is evidently improved as compared with polyaniline prepared in strong acids. This is due to the fact that H_2PO_4^- ions doped in polyaniline and the electrolytic solution of NaH_2PO_4 play an important role in adjusting the pH value at the electrode surface. Thus, the use of an anion possessing buffer capacity as dopant anion is a preferable strategy for extending the applicable pH region of polyaniline. The FTIR spectra of PAn-P prove that the dopant anion in PAn-P is H_2PO_4^- . This is very favorable for stabilizing the electrochemical activity of PAn-P over a wider pH region, especially at higher pH values.

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