

ELECTROCHEMICAL COPOLYMERIZATION OF ANILINE AND AZURE B*

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Abstract The electrochemical copolymerization of aniline and *N,N,N'*-trimethylthionin (azure B) in aqueous solutions has been carried out using the potential sweep method. The optimum conditions for the coelectrodeposition are that the pH value and the temperature of the electrolytic solution are controlled at 5.57 and 30°C, respectively, and the scan potential range is set between -0.25 and 1.10 V (versus SCE). The copolymerization rate of aniline and azure B is about 3 times larger than that of aniline in the absence of azure B. The copolymerization of aniline and azure B was verified from the results of visible spectra during electrolysis, FTIR spectra and the atomic force microscopy (AFM) images of the polymers. The *in situ* visible spectrum for the electrolysis of the solution containing aniline and azure B is different from that of the respective aniline and azure B. The FTIR spectrum of the copolymer is not a superposition of that of polyaniline and poly(azure B). The AFM image of the copolymer is different from those of polyaniline and poly(azure B) and is not a mixture of individual polymers. The conductivity of the copolymer synthesized at pH 5.57 is four orders of magnitude higher than that of polyaniline synthesized under the same conditions, but in the absence of azure B. The electrochemical properties of the copolymer are mainly attributed to polyaniline, but the copolymer has a better electrochemical reversibility and a much faster charge transfer than those of polyaniline.

Keywords Aniline, Azure B, Electrochemical copolymerization, Characterization of copolymer, Electrochemical property

INTRODUCTION

Polyaniline has a number of advantages over other conducting polymers; its discharge capacity is greater than that of polypyrrole^[1]. Polyaniline film shows a swift change of color with potential^[2], a good photoelectrochemical conversion of light to electricity^[3, 4] and a rather porous structure^[5-7] compared with polypyrrole film^[8]. The latter characteristic can be employed to immobilize enzymes using a doping method^[7]. However, the electrochemical polymerization of aniline in solutions with lower acid concentration is very slow, and the polyaniline obtained in this manner has inferior properties. The optimum pH values for most enzymes are in the pH range of 4 to 10. To immobilize enzymes in polyaniline film, the polyaniline should have high electrochemical activity at higher pH values. Thus, it is of great importance to improve further the properties of polyaniline, so that we can extend its application. To attain this aim, the best way is to copolymerize aniline with other monomers.

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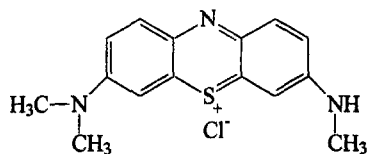
Among conducting polymers, the copolymerization of pyrrole and thiophene (or bithiophene)^[9-14] and the copolymerization of pyrrole and furan^[15] have been extensively investigated. In these papers, the copolymerization conditions, the properties and the characterization of the copolymers were reported. A main feature of the characterization is that the IR spectrum of the copolymer is not a superposition of those of the individual polymers.

Compared with pyrrole, the reports about the copolymerization of aniline and other monomers are scanty. One of the reasons is that the electrochemical polymerization of aniline in acid medium is fast, but it is very slow at pH > 1. Ruckenstein *et al.* reported the preparation of electrically conductive polyaniline-poly-styrene composites using an emulsion pathway^[16]. The composites prepared in this manner are not brittle and have an electrical conductivity as high as 3–5 S cm⁻¹. Talu *et al.* reported the copolymer of aniline and pyrrole, and the copolymerization was carried out via two steps, *i.e.*, polyaniline was synthesized first and pyrrole was polymerized afterwards^[17]. Bélanger *et al.* recently investigated the coelectropolymerization of pyrrole and aniline in organic acid medium^[18]. They found that the IR spectrum of the copolymer is not a simple superposition of the spectrum of each individual polymer. This means that the resulting polymer is a copolymer instead of a mixture of polypyrrole and polyaniline.

We found that azure B in the aqueous solutions with pH value between 2 and 11 can be oxidized and reduced reversibly around 0.1 V (versus SCE) and can be polymerized at potentials higher than 0.65 V (versus SCE)^[19, 20]. The oxidation polymerization potential of azure B is close to that of aniline. Therefore, it may be possible to copolymerize azure B with aniline. In this paper, we studied the coelectropolymerization of aniline and azure B in the aqueous solutions at pH 5.57, and characterized the copolymer by the measurement of conductivity, electrochemical properties, IR spectra, atomic force microscopy (AFM) image and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

The chemicals used were all reagent grades. *N,N,N'*-Trimethylthionin (azure B) was obtained from Sigma Co. Aniline was distilled before use. 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 that in the *in-situ* spectroelectrochemical experiment.



A Model HPD-1A potentiostat/galvanostat (Jilin Longjing, China) was used for cyclic voltammetry. The cyclic voltammograms were recorded using a YEW Model 3036 X-Y recorder (Yokogawa Hokushin Electric Co., Japan). The scan rate was 60 mV s⁻¹. The temperature for the polymerization of a mixture of aniline and azure B was controlled at 30°C. The polymer for the measurement of conductivity was thoroughly washed using hydrochloric acid solution at pH 3 to remove NaCl, unreacted aniline and azure B, and then dried at 70°C for 24 h. The conductivity of the polymers was measured on a pressed pellet using a four-probe technique. A Model MPS-2000 double-beam UV-Visible spectrometer (Shimadzu Co., Japan) was used for the spectroelectrochemical experiment, in which the electrolytic cell consisted of an ITO conducting glass working electrode, a platinum net counter electrode and an Ag/AgCl reference electrode (with saturated KCl solution). The electrolytic solution was put into both working and reference cells for the measurement of *in-situ* visible spectra during electrolysis. The XPS experiment of the polymer polymerized on platinum foil was carried out using a VG Scientific ESCA Lab 220i-XL equipment. IR spectra of all samples were measured on KBr pellets using a Nicolet 740 FTIR instrument. The AFM images of the polymers were recorded using a Nanoscope III atomic force microscope. All polymers for the AFM experiments were polymerized on the platinum foils.

RESULTS AND DISCUSSION

Effect of pH on the Film Growth of Polymers

Cyclic voltammetry was carried out to study the electrolysis of aniline in the solution containing 0.1 mol dm⁻³ aniline and 0.5 mol dm⁻³ NaCl with pH 3.55 or pH 5.57. In the cyclic voltammograms (CVs) of the solution with pH 3.55 (which is omitted here), there is an anodic peak at 0.80 V and a cathodic peak at 0.20 V in the first cycle, and then the anodic peak current decreases markedly in the subsequent cycles until the eightieth cycle. The result indicates that it is very difficult to grow polyaniline film in the solution with pH 3.55. The CVs in the solution with pH 5.57, as shown in Fig. 1, behave differently from that with pH 3.55. Before the twentieth cycle, the change of the current in the CVs is similar to that with pH 3.55. However after the twentieth cycle, the current increases with the number of cycles. A shoulder peak at 0.98 V appears for the eightieth cycle (curve 6 in Fig. 1). This means that polyaniline film can grow with time in the solution at pH 5.57.

The CVs (omitted here) in the solution containing 0.1 mol dm⁻³ aniline, 2.5 mmol dm⁻³ azure B and 0.5 mol dm⁻³ NaCl with pH 3.55 resemble that of the solution without azure B, *i.e.*, the presence of azure B does not affect the polymerization of aniline in this case.

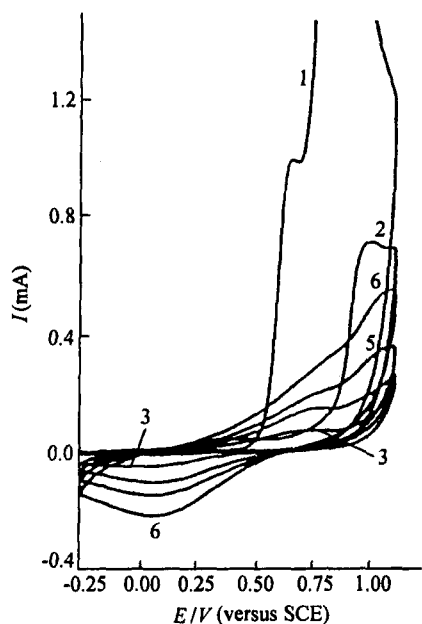


Fig. 1 Cyclic voltammograms of polyaniline film growth during electrolysis of the solution containing 0.1 mol dm⁻³ aniline and 0.5 mol dm⁻³ NaCl with pH 5.57
Curves: (1) first cycle, (2) second cycle, (3) twentieth cycle, (5) sixtieth cycle and (6) eightieth cycle, at 30°C

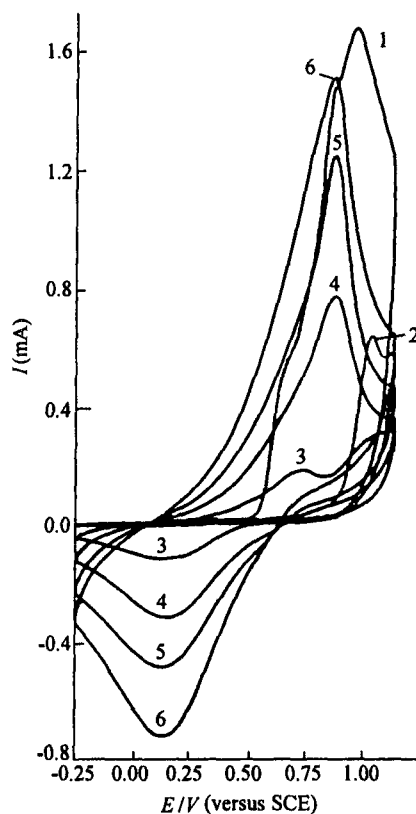


Fig. 2 Cyclic voltammograms of the polymer film growth during electrolysis of the solution containing 0.1 mol dm⁻³ aniline, 2.5 mmol dm⁻³ azure B and 0.5 mol dm⁻³ NaCl with pH 5.57
Curves: (1) first cycle, (2) second cycle, (3) twentieth cycle, (4) fortieth cycle, (5) sixtieth cycle and (6) eightieth cycle, at 30°C

Figure 2 shows the CVs in the solution containing 0.1 mol dm⁻³ aniline, 2.5 mmol dm⁻³ azure B and 0.5 mol dm⁻³ NaCl with pH 5.57. Before the twentieth cycle, the current also decreases with increasing number of

cycles. Nevertheless, in the twentieth cycle a new anodic peak at 0.7 V and a cathodic peak at 0.13 V appear (see curve 3), then the peak currents start to increase with increasing number of cycles. The anodic peak appears at 0.8 V in the eightieth cycle (see curve 6 in Fig. 2), which is lower than that in the absence of azure B as shown in Fig. 1. The anodic peak current of curve 6 in Fig. 2 is about 3 times larger than that in Fig. 1 for the eightieth cycle. These results indicate that azure B may play some role for the electrochemical catalysis. In addition, the difference between Fig. 1 and Fig. 2 may be caused by the electrochemical copolymerization of aniline and azure B. Also, the CVs in Fig. 2 are much different from those of the electrochemical polymerization of azure B, in which a pair of redox peaks appears around 0 V (versus SCE)^[20].

We found that the polymerization rate of aniline at pH > 6 is lower than that at pH 5.57 in the absence and presence of azure B. Based on the above results, the solutions with pH 5.57 will be used to prepare the polymers in the following experiments.

In-Situ Visible Spectra During Electrolysis

Figure 3 shows the visible spectra during the electrolysis of the solution containing 0.1 mol dm⁻³ aniline and 0.5 mol dm⁻³ NaCl with pH 5.57. The measurements were carried out at an interval of 4 min between two measurements. The potential scan rate was controlled at 60 mV s⁻¹ during the *in-situ* spectroelectrochemical experiments. The scan potential range was set between -0.25 and 1.10 V. The absorption between 430 and 900 nm increases with potential cycles, but no peak appear during electrolysis for 32 min. After the electrolysis, a shallow yellow film was found on the ITO conducting glass, which is polyaniline.

Figure 4 shows the visible spectra during electrolysis of the solution containing 2.5 mmol dm⁻³ azure B, 0.2 mol dm⁻³ NaH₂PO₄ and 0.5 mol dm⁻³ NaCl with pH 5.57. The measurements were carried out at an interval of 3 min between two measurements. It is clear that a peak at 725 nm appears on curve 1 for the first cycle, and then its absorbance increases with the number of potential cycles. After electrolysis, a blue film was found on the ITO electrode, which is poly(azure B).

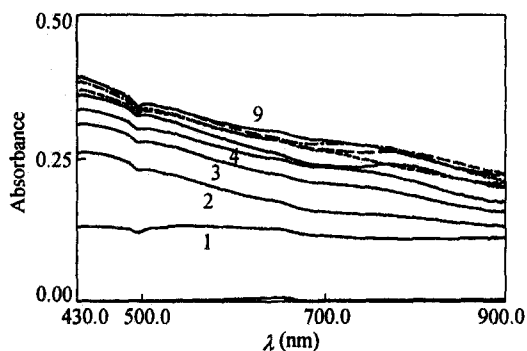


Fig. 3 Relationship between visible spectra and time during electrolysis of the solution of 0.1 mol dm⁻³ aniline and 0.5 mol dm⁻³ NaCl with pH 5.57
Curves: (1) starting electrolysis, (2) 4 min, (3) 8 min and (9) 32 min

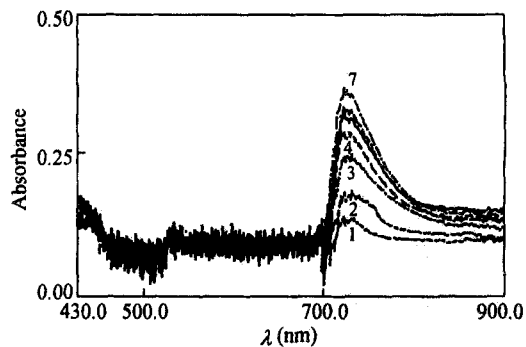


Fig. 4 Relationship between visible spectra and time during electrolysis of the solution of 2.5 mmol dm⁻³ azure B, 0.2 mol dm⁻³ NaH₂PO₄ and 0.5 mol dm⁻³ NaCl with pH 5.57
Curves: (1) starting electrolysis, (2) 3 min, (3) 6 min and (7) 21 min

Figure 5 shows the visible spectra during electrolysis of the solution containing 0.1 mol dm⁻³ aniline, 2.5 mmol dm⁻³ azure B and 0.5 mol dm⁻³ NaCl with pH 5.57. The measurements were carried out at an interval of 2 min between two measurements. A peak at 730 nm appears on curve 1 for the first cycle, and then this peak becomes more pronounced as the number of cycles increases; finally, this peak shifts to 760 nm. Its absorbance increases more quickly than those in Fig. 3 and Fig. 4. This result confirms that the polymerization rate of aniline in the presence of azure B is faster than those of the electrolysis of each individual aniline and azure B, which is in good agreement with the CVs of the electropolymerization on platinum foil shown in Fig. 1 and Fig. 2.

Comparing Fig. 5 with Fig. 3 and Fig. 4, we can see that the spectra in Fig. 5 are not a superposition of those of polyaniline and poly(azure B). Based on these visible spectra, we conclude that the product obtained from electrolysis of the mixed solution of aniline and azure B is a copolymer, not a mixture of polyaniline and poly(azure B).

FTIR Spectra

Figure 6 shows the FTIR spectra of polyaniline (curve 1), copolymer (curve 2) and poly(azure B) (curve 3), respectively. Curve 1 in Fig. 6 is a typical spectrum of polyaniline^[21, 22], in which the band at 3450 cm^{-1} can be assigned as the stretching vibrations of N—H. The 3408 cm^{-1} band and the small shoulder peak at 3063 cm^{-1} in curve 3 are ascribed to the stretching vibrations of O—H group from water^[19] and the stretching vibrations of C—H in $-\text{CH}_3$ group of azure B, respectively. However, in the spectrum of copolymer (curve 2), the 3450 cm^{-1} band does not exist. Presumably, the copolymerization took place through the connection of terminal group $-\text{NH}$ in polyaniline with the $-\text{NH}(\text{CH}_3)$ in azure B to form the chain, followed by the chain propagation along aniline units.

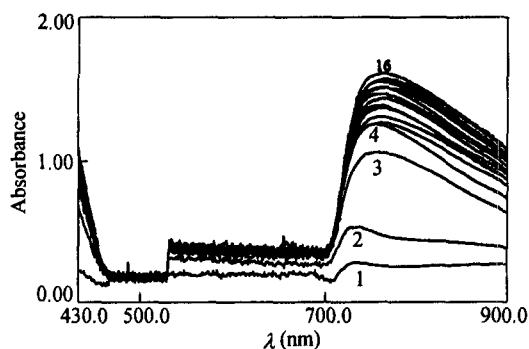


Fig. 5 Relationship between visible spectra and time during electrolysis of the solution containing 0.1 mol dm^{-3} aniline, 2.5 mol dm^{-3} azure B and 0.5 mol dm^{-3} NaCl with pH 5.57

Curves: (1) starting electrolysis, (2) 2 min, (3) 4 min and (16) 36 min

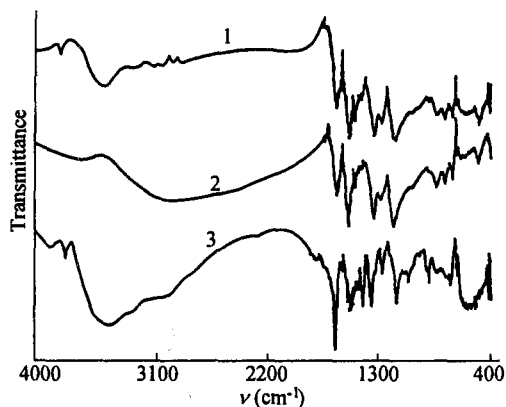


Fig. 6 FTIR spectra of polyaniline (1), copolymer (2) and poly(azure B) (3)

AFM Images of the Polymers

Figure 7(a) shows the AFM image of polyaniline film, which consists of globular particles with a diameter of $0.2\text{--}0.3\text{ }\mu\text{m}$. Figure 7(b) shows the image of poly(azure B) film, which has a more regular arrangement of fibrous particles with a diameter of $0.1\text{--}0.2\text{ }\mu\text{m}$. Figure 7(c) shows the image of the copolymer, in which most of the surface is covered with a net structure. The morphology of the copolymer is different from that of polyaniline and poly(azure B), and also it is not a superposition of each individual polymer. The AFM observation confirms further that the electrochemical copolymerization of aniline and azure B does take place.

XPS of the Copolymer

The copolymer for the XPS experiment was obtained from the electrolysis of a mixture solution of aniline and azure B, and was then reduced at -0.3 V in 0.1 mol dm^{-3} NaCl with pH 3.8 for 30 min. The purpose of the reduction is to remove chloride ions doped in the copolymer during electropolymerization. After reduction, the copolymer film was washed thoroughly using doubly distilled water. The XPS of the polymer, as shown in Fig. 8, indicates that there are C, N, S, Cl and O atoms in the copolymer. C and N atoms come from aniline and azure B. Oxygen atoms may be attributed to the oxygen and water adsorbed in the copolymer, like that in polyaniline detected by XPS^[23]. Sulfur atoms in the copolymer come from azure B. The presence of S atoms in the

copolymer confirms that there are azure B units in the copolymer chain.

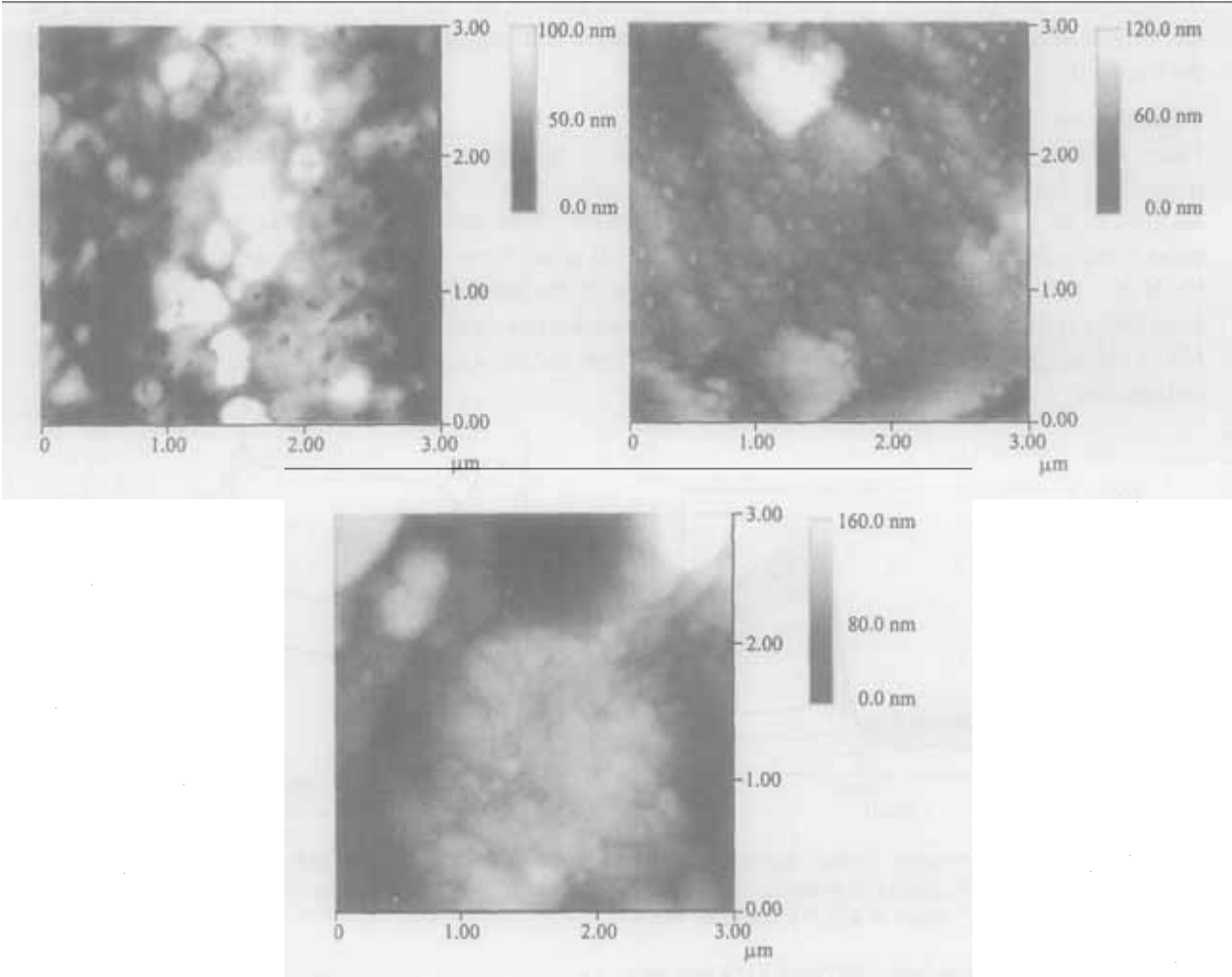


Fig. 7 AFM images of polymers, (a) polyaniline, (b) poly(azure B) and (c) copolymer

The C_{1s} peak in the XPS spectra of polyaniline is generally split into three peaks in the binding energy range between 284 and 288 eV^[24, 25]. However, the C_{1s} peak in the spectra of Fig. 8(a) is split into four peaks. The positions and relative intensity of the C_{1s} peaks are listed in Table 1.

Table 1. Peak positions of C_{1s} peaks	
Binding energy (eV)	Relative intensity (%)
288.8	5.45
287.7	10.14
286.0	18.50
284.6	65.91

The peak with the binding energy 288.8 eV may be attributed to the carbon atom in azure B. Since some of the carbon atoms in azure B are attached to an electro-negative nitrogen or sulfur atom, *i.e.*, the chemical environment of C atoms in azure B is different from that of C atoms in polyaniline. Both of the N and S atoms play a direct and indirect role in decreasing the shielding of the positive nuclear charges of C_{1s} by outer electrons. Thus the effective attractive force of the nucleus with regard to the core electrons of C_{1s} is increased, *i.e.*, its binding energy should be higher than those of other carbon atoms in the copolymer. In addition, the content of

the C atoms having 288.8 eV is the lowest among the four kinds of C_{1s} , which is also evidence for C_{1s} coming from azure B.

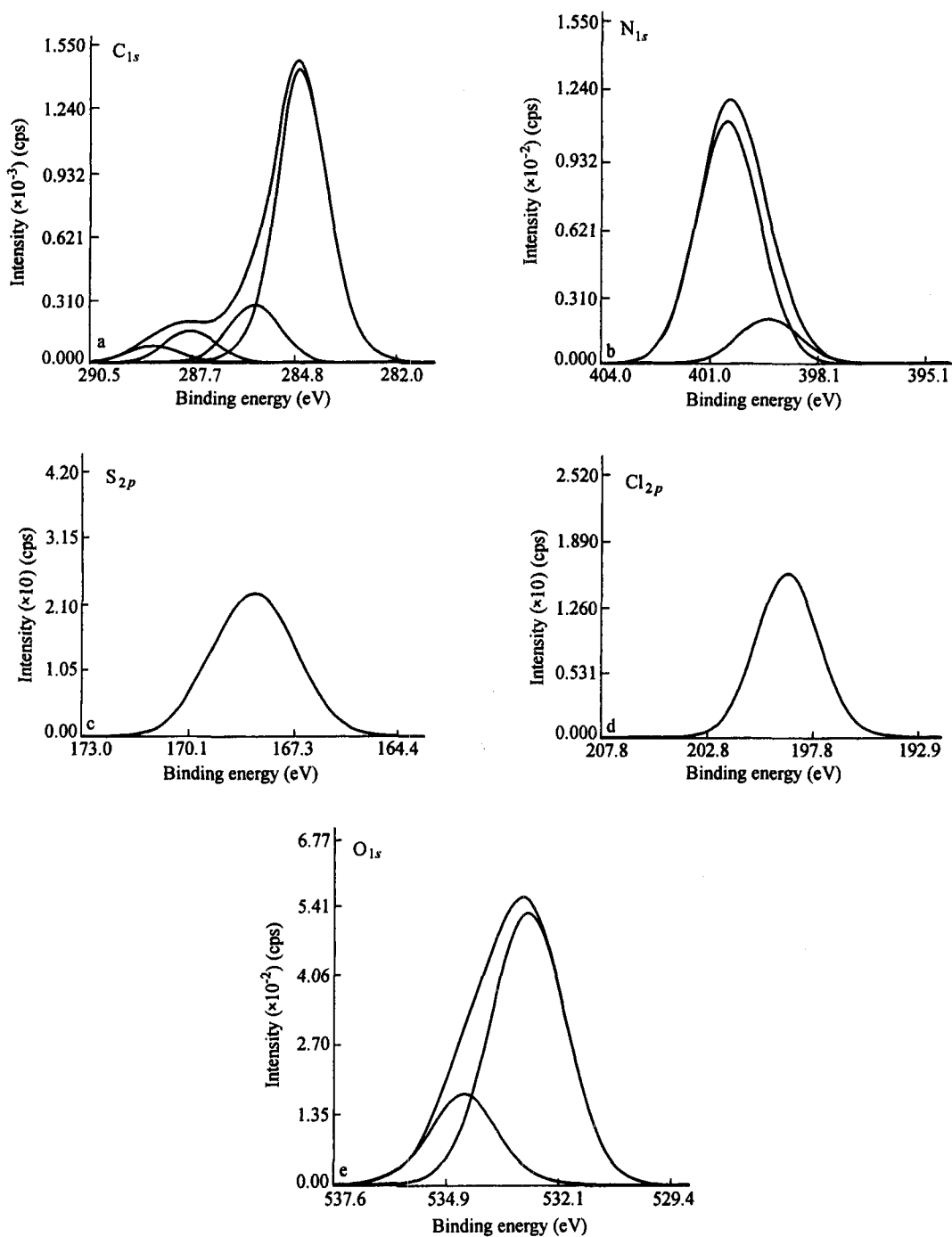


Fig. 8 XPS spectra of the copolymers

The value of binding energy in Fig. 8(d) indicates that chlorine is present in the copolymer. The relative content of the chlorine atom is only 0.29%, which is the least among the elements contained in the copolymer.

The small amount of chlorine atom may come from the Cl^- counter anions remaining in the copolymer after the reduction treatment of the sample.

Conductivity

The polymer samples for the conductivity measurement were synthesized in solution at pH 5.57 with a potential sweep method. The conductivity of the copolymer prepared between -0.25 and 1.10 V is $1.02 \times 10^{-2} \text{ S cm}^{-1}$, and that of the copolymer synthesized between -0.25 and 1.2 V is $2 \times 10^{-3} \text{ S cm}^{-1}$. The latter is about one order lower than the former, which is probably caused by the over-oxidation of the copolymer at ca. 1.20 V during its electropolymerization. The conductivity of polyaniline, synthesized in the potential range between -0.25 and 1.10 V, is $3.9 \times 10^{-6} \text{ S cm}^{-1}$. Obviously, the conductivity of the copolymer is much higher than that of polyaniline synthesized in the same conditions. And it is also higher than that of poly(azure B) which is $10^{-4} \text{ S cm}^{-1}$ [20]. This result may be due to the fact that the polymerization rate of aniline in the presence of azure B (Fig. 2) is faster than that without azure B (Fig. 1). This means that the polymerization rate may affect the conductivity of the polymer film itself. It is well known that the conductivity of polyaniline is strongly affected by the pH values of the solution used in the polymerization[26]. The conductivity of the polyaniline synthesized in the solution at higher pH values is lower, which may be caused by the hydrolysis of imine-carbon bonds in polyaniline during the polymerization process at the higher pH values. In the copolymer, the hydrolysis of imine-carbon bonds would be inhibited to a certain extent. Thus the conductivity of the copolymer synthesized at pH 5.57 is much higher than that of polyaniline synthesized under the same conditions, and azure B plays an important role in raising the conductivity of the copolymer.

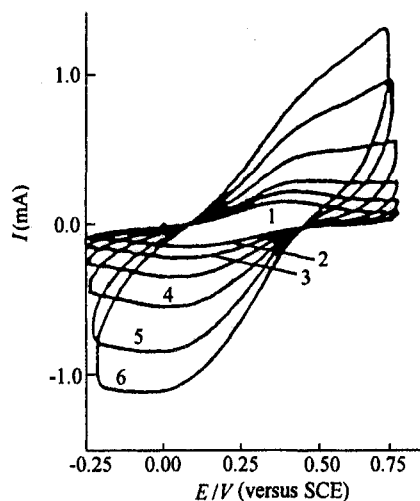


Fig. 9 Effect of scan rate on the cyclic voltammograms of polyaniline film in the solution of $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ and $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ with pH 2.0, scan rate mV s^{-1}
Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400 and (6) 600

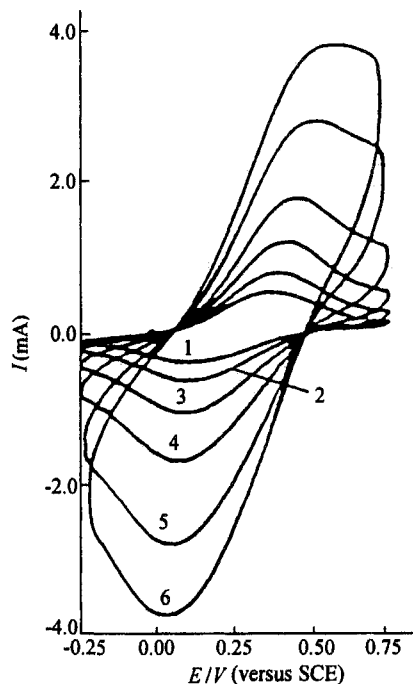


Fig. 10 Effect of the scan rate on the cyclic voltammograms of the copolymer film in the solution of $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ and $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ with pH 2.0, scan rate mV s^{-1}
Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400 and (6) 600

Effect of Scan Rate on the CVs of Polyaniline and Copolymer

Figure 9 and Fig. 10 show the CVs of the polyaniline film and the copolymer film in the solution of 0.2 mol dm^{-3} NaH_2PO_4 and 0.5 mol dm^{-3} NaCl with pH 2.0 at various scan rates, respectively. The two polymer films were prepared using the potential sweep method between -0.25 and 1.10 V for 80 cycles. In the CVs of polyaniline (Fig. 9), there is an anodic peak at 0.4 V and a cathodic peak at 0.1 V at a scan rate lower than 100 mV s^{-1} . When the scan rate was over 100 mV s^{-1} , the CV no longer shows a peak, but changes to an S-shaped curve with a current plateau. This means that the reaction is controlled by the electrode kinetics at a scan rate greater than 100 mV s^{-1} . In the CVs of the copolymer (Fig. 10), it is the same as that of polyaniline at a scan rate lower than 100 mV s^{-1} , which indicates that the electrochemical property of the copolymer is mainly dependent on that of polyaniline. But the CV curve at higher than 100 mV s^{-1} , which still shows a pronounced anodic peak and a cathodic peak even at a scan rate of 600 mV s^{-1} (curve 6 in Fig. 10), is different from that of polyaniline. This indicates that the electrode reaction rate of the copolymer is more rapid than that of polyaniline. The ratio of the anodic peak current to the cathodic peak current is near unity at various scan rates, and the position of the cathodic peak hardly changes with scan rate. Therefore, the copolymer has a rather good electrochemical reversibility at pH 2. In comparison with the CVs in Fig. 9, the area of the CVs in Fig. 10 is about 3 times larger at the same scan rate. This is caused by the thicker film of the copolymer compared to polyaniline. The result is in good agreement with the film growth rates of polyaniline (see Fig. 1) and the copolymer (see Fig. 2).

CONCLUSION

The experimental results indicate that aniline can be polymerized electrochemically in solutions with a pH value lower than 6, but its polymerization rate becomes much lower at higher pH values. However, the polymerization rate of aniline in the presence of azure B at pH 5.57 is increased markedly. This is caused by the copolymerization of aniline and azure B. The copolymerization is affected strongly by pH value and working electrode potential. The copolymerization of aniline and azure B is evidenced by the measurements of *in-situ* visible spectra during electrolysis, FTIR spectra and AFM images of polyaniline, poly(azure B) and copolymer. The conductivity of the copolymer synthesized at pH 5.57 is four orders of magnitude higher than that of polyaniline synthesized under the same conditions. The electrochemical properties of the copolymer are mainly contributed by polyaniline, but the copolymer has a better electrochemical reversibility, and has a much faster charge transfer than that of polyaniline at pH 2. The composition of the copolymer is very complicated, and needs further study.

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