

ELECTROCHEMICAL SYNTHESIS AND PROPERTIES OF POLY(AZURE B)*

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Abstract A blue poly(azure B) film has been synthesized using repeated potential cycling between -0.25 and 1.10 V (versus SCE). The electrolytic solution consisted of 2.5 mmol dm^{-3} azure B, 0.5 mol dm^{-3} NaCl and 0.2 mol dm^{-3} NaH_2PO_4 at the pH range of 2.0 to 11.0. The *in situ* visible spectrum during electrolysis of azure B shows that the intensity at 740 nm peak increases with increasing numbers of potential cycles, which is attributable to the formation of poly(azure B). The wavelength of its corresponding absorption peak is 98 nm longer than that of azure B. The polymerization rate is strongly affected by pH values. The anodic peak potential and cathodic peak potential of the poly(azure B) in a solution of pH 3.0 are not affected by increasing the scan rate from 25 to 600 mV s^{-1} . Poly(azure B) has good electrochemical reversibility and fast charge transfer characteristic in the pH range of 2.0 and 11.0. The conductivity of poly(azure B) is $1.5 \times 10^{-4} \text{ S cm}^{-1}$. According to the differences between FTIR spectra of poly(azure B) and azure B, an electrochemical polymerization mechanism of azure B is proposed in this paper.

Keywords Azure B, Electrochemical polymerization, Electrochemical properties, Conductivity, *In situ* UV-visible spectra, FTIR spectra

INTRODUCTION

The interesting discovery about the interconversion of metallic and insulating forms of polyacetylene^[1] has played an important role in synthesis and applications of conducting polymers. Since then, many conducting polymers have been synthesized, such as polypyrrole^[2], polyaniline^[3], polythiophene^[4], poly(*p*-phenylene)^[5], polyazulene^[6], polyfuran^[6] and polyfluorene^[7]. Conducting polymers can be used for battery electrodes^[8-11], electrochromic devices^[12-14], light-emitting diodes^[15, 16] and immobilization of enzymes^[17, 18]. The different applications need conducting polymers having different properties. Thus, the synthesis of new types of conducting polymers is very important in the field of material sciences. Some of the indicators and dyes can be oxidized or reduced. This means that some of them may be polymerized electrochemically. Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new systems^[19]. Therefore, we used the potential sweep method to study the electrochemical polymerization of a series of indicators and dyes. The advantage of this method is that it is quick to verify whether or not the electrochemical polymerization of a monomer takes place. Among the indicators and dyes under investigation, azure B was found to be polymerized electrochemically.

In this paper, we report the conditions for the electrochemical polymerization of azure B, the electrochemical properties, conductivity, UV-visible spectra and FTIR spectra of poly(azure B).

EXPERIMENTAL

Azure B was obtained from Sigma Company. Other chemicals used in this work were reagent grade. Doubly distilled water was used to prepare solutions. The electrolysis cell consisted of two platinum foils and a reference

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electrode, and the area of the working electrode was $4 \times 4 \text{ mm}^2$. Potentials given here are referred to the saturated calomel electrode (SCE), but in the *in situ* determination of visible spectra during electrolysis of azure B, a Ag/AgCl (with saturated KCl solution) electrode was used as the reference electrode.

A DH-1 potentiostat-galvanostat was used for the cyclic voltammetry. A YEW Model 3036 X-Y recorder was used to record the cyclic voltammograms. A PAR Model 173 potentiostat-galvanostat with a Model 179 digital coulometer was used for the electrochemical polymerization at a constant potential. The temperature of the electrolysis was controlled at 25°C . The *in situ* spectroelectrochemical experiment during electrolysis of azure B and the measurement of the UV-visible spectra of poly(azure B) polymerized on an indium-tin oxide (ITO) conducting glass were carried out using a MPS-2000 double-beam spectrometer. The electrolytic cell for the *in situ* spectroelectrochemical experiment consisted of an ITO conducting glass, a platinum net and a Ag/AgCl electrode (with saturated KCl solution). FTIR spectra of azure B and poly(azure B) were measured on pressed pellets with KBr using a Nicolet 740 FTIR spectrometer. The conductivity of poly(azure B) was measured on a pressed pellet using a four-probe technique.

RESULTS AND DISCUSSION

Effect of pH on the Polymerization of Azure B

The electrolytic solution consisted of 2.5 mmol dm^{-3} azure B, 0.2 mol dm^{-3} NaH_2PO_4 and 0.5 mol dm^{-3} NaCl. The pH values of the electrolytic solution used were controlled between 2.0 and 11.0. The electrolysis of azure B was carried out using repeated potential cycling at each pH unit interval from pH 2.0 to 11.0. The sweeping potential range was set between -0.25 and 1.10 V . The scan rate was 60 mV s^{-1} . Here we present the cyclic voltammograms of film growth during electrolysis of azure B solution with pH 2.0, 4.0 and 11.0. The cyclic voltammograms of film growth at other pH values are omitted.

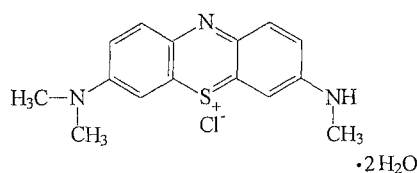
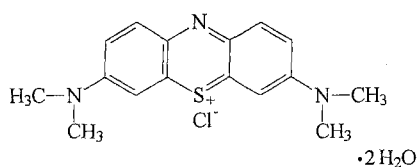
The cyclic voltammograms of film growth during the electrolysis of the solution of azure B at pH 2.0 are shown in Fig. 1, in which *I-E* curves of the first cycle (curve 1) to thirtieth cycle (curve 5) are recorded. From Fig. 1, we can see an anodic peak at 0.09 V and a cathodic peak at 0.05 V for the first cycle. The potential of the anodic peak shifts towards positive potentials with increasing numbers of potential cycles, however, the potential of the cathodic peak is almost independent of potential cycles. Both the anodic peak current and cathodic peak current change a little during 30 cycles. After electrolysis, a pale blue film, i.e., poly(azure B), was formed on the working electrode.

Figure 2 shows the cyclic voltammograms of polymer film growth during electrolysis of azure B solution at pH 4.0 having an anodic peak at -0.10 V and a cathodic peak at -0.15 V for the first cycle (curve 1). It is clear that its anodic peak potential is more negative than that in Fig. 1. In comparison with Fig. 1, the potential of the anodic peak in Fig. 2 shifts towards positive potentials more slowly with increasing numbers of potential cycles. Both the anodic peak current and cathodic peak current increase with increasing numbers of potential cycles, which is quite different from film growth at pH 2.0 in Fig. 1. This indicates that the rate of polymerization of azure B is faster at pH 4.0 than that at pH 2.0. After electrolysis, a deep blue film was formed on the working electrode.

Figure 3 depicts the cyclic voltammograms of polymer film growth during electrolysis of azure B solution at pH 11.0. It is clear that the wave shapes of *I-E* curves in Fig. 3 are much different from those in Fig. 1 or in Fig. 2, and the anodic current at about 1 V decreases with increasing numbers of potential cycles, while the cathodic current at about -0.24 V increases first, and then decreases with increasing numbers of potential cycles during the electrolysis process. After electrolysis, a blue film was also formed on the working electrode.

The effect of potential on the polymerization of azure B has been tested. It was found that azure B can be polymerized when the potential is greater than 0.65 V .

The above results indicate that azure B can be polymerized electrochemically over a wide pH range, since its structure is similar to that of methylene blue. Methylene blue can be polymerized electrochemically, which has been reported^[20-22].



The conductivity of poly(azure B) was measured on a pressed pellet, which is $1.5 \times 10^{-4} \text{ S cm}^{-1}$ pressed pellet. The conductivity of poly(azure B) is slightly affected by the pH value of the electrolytic solution used in the synthesis of poly(azure B). The conductivity of poly(azure B) prepared at pH 2.0 and pH 11.0 is the lowest among other poly(azure B) prepared at the pH range of 2.0 to 11.0.

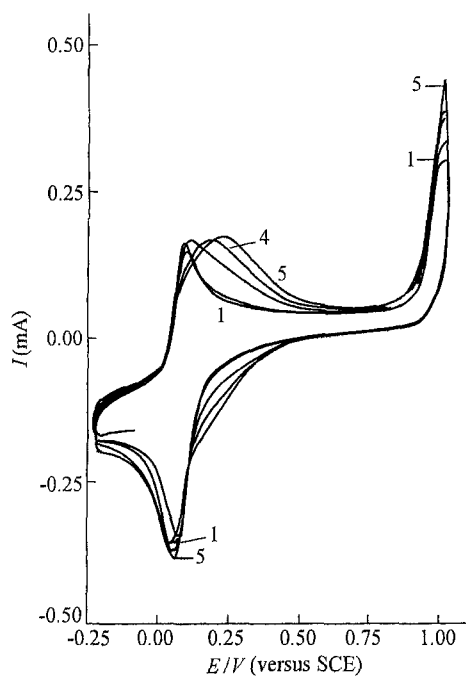


Fig. 1 Film growth of poly(azure B) during the electrolysis of the solution consisting of 2.5 mmol dm^{-3} azure B, $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ with pH 2.0

Curves: (1) first cycle, (4) twentieth cycle, (5) thirtieth cycle, at 25°C

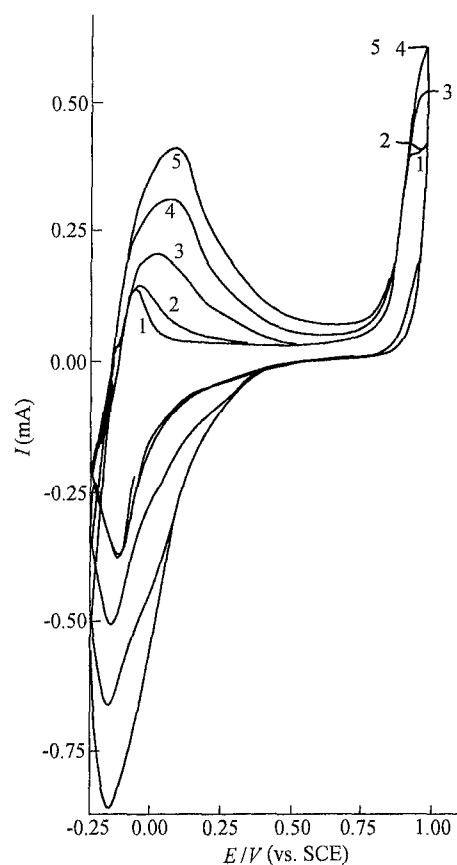


Fig. 2 Film growth of poly(azure B) during the electrolysis of the solution consisting of 2.5 mmol dm^{-3} azure B, $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ with pH 4.0

Curves: (1) first cycle, (2) second cycle, (3) tenth cycle, (4) twentieth cycle, (5) thirtieth cycle, at 25°C

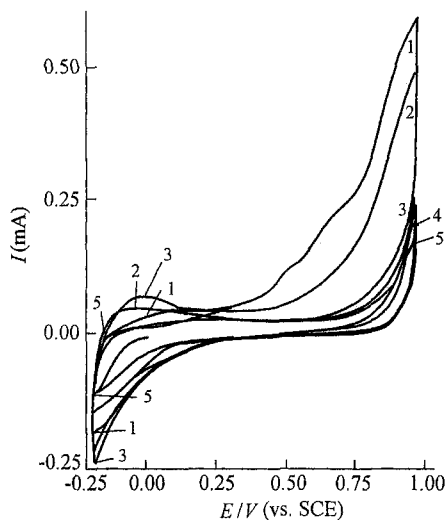


Fig. 3 Film growth of poly(azure B) during the electrolysis of the solution consisting of 2.5 mmol dm^{-3} azure B, 0.5 mol dm^{-3} NaCl and 0.2 mol dm^{-3} Na_2HPO_4 with pH 11.0

Curves: (1) first cycle, (2) second cycle, (3) tenth cycle, (4) twentieth cycle, (5) thirtieth cycle, at 25°C

Visible Spectra of Poly(azure B)

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 . Figure 4 shows the variation of visible spectra during electrolysis of the solution containing 2.5 mmol dm^{-3} azure B, 0.2 mol dm^{-3} Na_2HPO_4 and 0.5 mol dm^{-3} NaCl with pH 4.0, which was also used as the reference solution of measurements of spectra. The measurements were carried out at an interval of 3 min between two measurements. In Fig. 4, the intensity of the peak at 740 nm increases with increasing numbers of potential cycles. This peak is attributed to the formation of poly(azure B), since a blue film was found on the ITO conducting glass after electrolysis.

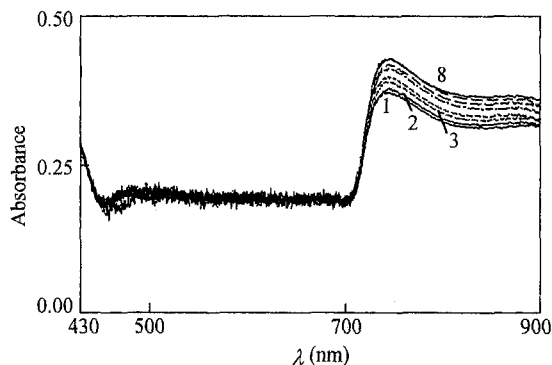


Fig. 4 Variation of visible spectrum with time during electrolysis of the solution containing 2.5 mmol dm^{-3} azure B, 0.2 mol dm^{-3} Na_2HPO_4 and 0.5 mol dm^{-3} NaCl with pH 4.0

Curves: (1) starting electrolysis, (2) 3 min, (3) 6 min, (8) 21 min

Figure 5 shows the visible spectra of azure B solution and dried poly(azure B) film deposited on an ITO conducting glass. Curve 1 and curve 2 are the visible spectra of 6.25×10^{-3} and $2.5 \times 10^{-2} \text{ mmol dm}^{-3}$ azure B in the solution of 0.2 mol dm^{-3} Na_2HPO_4 and 0.5 mol dm^{-3} NaCl with pH 4.0, respectively. The shape of the lines in

Fig. 5 is affected by the concentration of azure B, but they all have a same absorption peak at 642 nm. The peak position and the shape of curve 2 are the same as those of the standard visible spectrum of azure B^[23]. As mentioned above, the absorption peak of poly(azure B) appears at 740 nm (in Fig. 4), about 98 nm longer than that of the monomer, azure B, because the polymer is constituted of several monomers. However, the absorption peak of the dried poly(azure B) film polymerized on an ITO conducting glass shifts to 690 nm (curve 3 in Fig. 5), which is even longer than that of the monomer (curves 1 and 2 in Fig. 5), but less than that of poly(azure B) deposited on the ITO conducting glass determined during the electrolysis process (Fig. 4). This shift is presumably caused by the solvent effect. In general, a polar solvent causes the absorption band of $\pi \rightarrow \pi^*$ transition to shift towards longer wavelengths. Water is a strong polar solvent, which affects the $\pi \rightarrow \pi^*$ transition in poly(azure B). As a result, the absorption wavelength of poly(azure B) is longer in the aqueous solution than in a dried film.

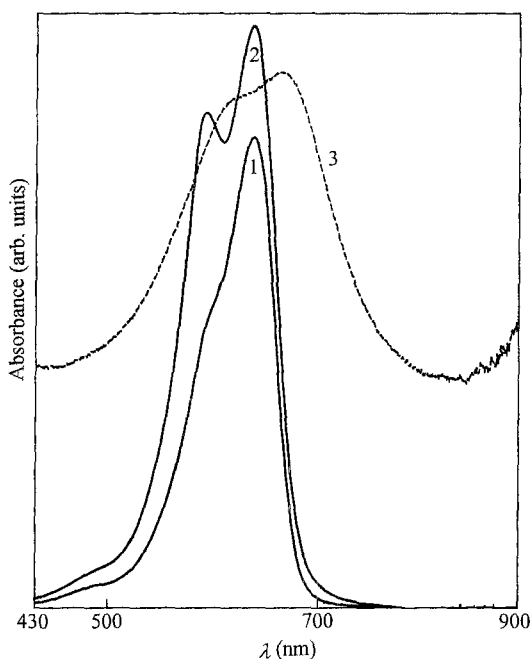


Fig. 5 Visible spectra of azure B solution and dried poly(azure B) film deposited on an ITO conducting glass

Curves: (1) 6.25×10^{-3} mmol dm^{-3} azure B, 0.2 mol dm^{-3} NaH_2PO_4 and 0.5 mol dm^{-3} NaCl, pH 4.0, (2) 2.5×10^{-2} mmol dm^{-3} azure B, 0.2 mol dm^{-3} NaH_2PO_4 and 0.5 mol dm^{-3} NaCl, pH 4.0, (3) dried poly(azure B) film

Cyclic Voltammograms of Poly(azure B) Obtained at Different pH Values

All poly(azure B) films used in the following experiments were obtained using repeated potential cycling for 30 cycles. Figure 6 shows the effect of pH value on the cyclic voltammograms of poly(azure B) synthesized in the solution at pH 4.0. The scan rate was 60 mV s^{-1} . Cyclic voltammetry was carried out in a solution consisting of 0.5 mol dm^{-3} NaCl and 0.2 mol dm^{-3} NaH_2PO_4 at pH 2.0 to 11.0. In Fig. 6, both the anodic peak potential and cathodic peak potential shift towards negative potentials by about 60 mV per unit pH as pH increases from 2.0 (curve 1) to 4.0 (curve 3), and then this shift decreases continuously from pH 5.0 (curve 4) to 11.0 (curve 10). This means that the redox process of the polymer is related to proton concentration of the solution, i.e., protons in the polymer enter into the solution for the oxidation process, and vice versa for the reduction process. Both the anodic peak current and cathodic peak currents are slightly affected by pH value in the range of 2.0 and 11.0.

This result is different from that of polyaniline. The electrochemical activity of polyaniline decreases with increasing pH values and is completely lost at pH 6.0^[24].

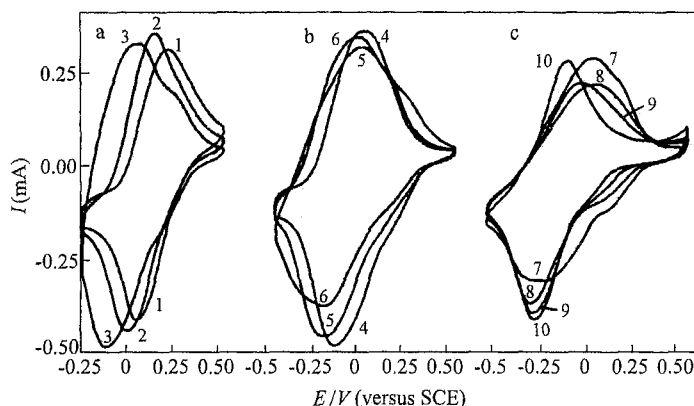


Fig. 6 Effect of pH value on cyclic voltammograms of poly(azure B) in the solution of 0.5 mol dm^{-3} NaCl and 0.2 mol dm^{-3} NaH_2PO_4 , poly(azure-B) synthesized at pH 4.0
Curves: (1) pH 2.0, (2) pH 3.0, (3) pH 4.0, (4) pH 5.0, (5) pH 6.0, (6) pH 7.0, (7) pH 8.0, (8) pH 9.0, (9) pH 10.0, (10) pH 11.0, at 25°C

After recording the cyclic voltammogram of poly(azure B) in the solution of pH 11.0, poly(azure B) was put into the solution of pH 2.0, the cyclic voltammogram was recorded again (omitted here). Its I - E on the cyclic voltammogram is the same as those of curve 1 in Fig. 6. This means that poly(azure B) has a good electrochemical reversibility and stability in the pH range of 2.0 to 11.0.

The cyclic voltammetry of poly(azure B) prepared at pH 2.0 was conducted in the above pH range (omitted here). The peak potential dependence of pH value and I - E wave shapes of poly(azure B) prepared at pH 2.0 are similar to those shown in Fig. 6.

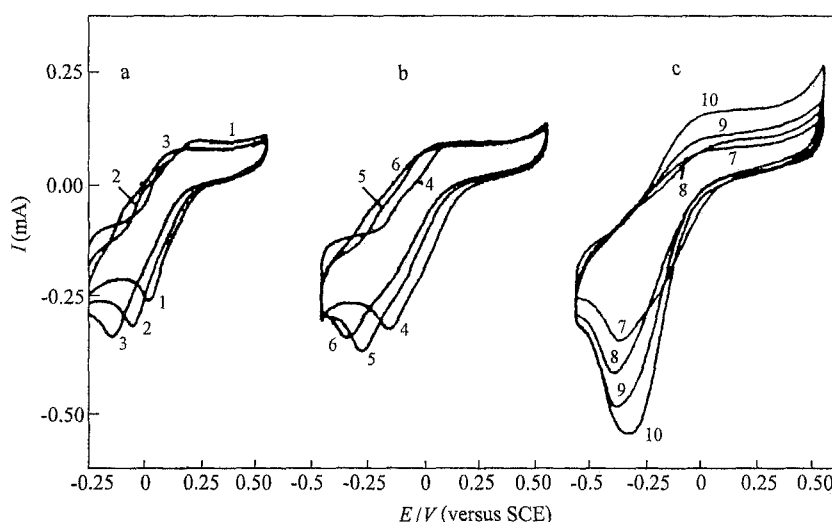


Fig. 7 Effect of pH value on cyclic voltammograms of poly(azure B) in the solution of 0.5 mol dm^{-3} NaCl and 0.2 mol dm^{-3} NaH_2PO_4 , the polymer synthesized at pH 11.0
Curves: (1) pH 2.0, (2) pH 3.0, (3) pH 4.0, (4) pH 5.0, (5) pH 6.0, (6) pH 7.0, (7) pH 8.0, (8) pH 9.0, (9) pH 10.0, (10) pH 11.0, at 25°C

Figure 7 shows the effect of pH value on the cyclic voltammograms of poly(azure B) synthesized in the electrolytic solution with pH 11.0. The I - E curves in Fig. 7 no longer show an anodic peak at each pH value. This electrochemical behavior is rather different from those shown in Fig. 6. The above results indicate that the electrochemical polymerization of azure B and the electrochemical properties of poly(azure B) are affected by the pH value of the electrolytic solution.

Figure 8 shows the cyclic voltammograms of poly(azure B) films in $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4$ with pH 3.0. All the poly(azure B) films used in this experiment were prepared at various pH values. From the areas of cyclic voltammograms, we can see that the electrochemical activity of poly(azure B) prepared at pH 4.0, i.e., the redox charge of poly(azure B) is the largest and is the smallest prepared at pH 2.0. The order of the redox charge of (Q) of poly(azure B) prepared at various pH values is as follows:

$$Q_{(\text{pH } 4.0)} > Q_{(\text{pH } 5.0)} > Q_{(\text{pH } 7.0)} > Q_{(\text{pH } 9.0)} > Q_{(\text{pH } 11.0)} > Q_{(\text{pH } 2.0)}$$

This difference may be caused by the film thickness or the electrochemical activity of poly(azure B) itself. The growth of film is very slow for electrolysis of azure B at pH 2.0 as shown in Fig. 1. Thus, this film is very thin compared with other films prepared at other pH values, which leads to low redox charge. To verify further, the polymerization of azure B at pH 2.0, 4.0, 8.0 and 11.0 was carried out at a constant potential of 1.10 V. The quantity of electricity passed during the electrolysis of each solution with different pH values was all 7.7×10^{-3} coulombs. Figure 9 shows the cyclic voltammograms of poly(azure B) films in a solution consisting of $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ with pH 3.0. From Fig. 9, we can see that the redox charge of poly(azure B) prepared at pH 4.0 is still the largest among other poly(azure B) films. The order of the redox

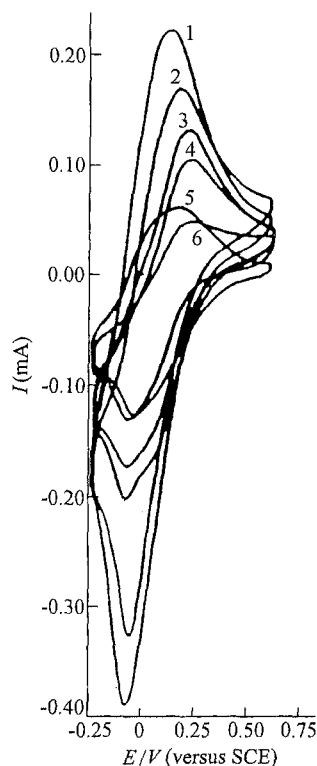


Fig. 8 Cyclic voltammograms of poly(azure B) films in $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4$ with pH 3.0.

Poly(azure B) films prepared at various pH values
Curves: (1) pH 4.0, (2) pH 5.0, (3) pH 7.0, (4) pH 9.0, (5) pH 11.0, (6) pH 2.0

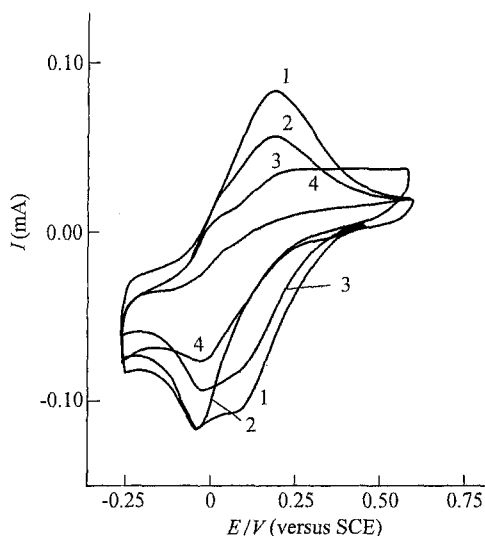


Fig. 9 Cyclic voltammograms of poly(azure B) films in the solution consisting of $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ with pH 3.0

Poly(azure B) films prepared at a constant potential and at various pH values
Curves: (1) pH 4.0, (2) pH 2.0, (3) pH 8.0, (4) pH 11.0

charge (Q) of poly(azure B) prepared at a constant potential and at different pH values is as follows:

$$Q_{(\text{pH } 4.0)} > Q_{(\text{pH } 2.0)} > Q_{(\text{pH } 8.0)} > Q_{(\text{pH } 11.0)}$$

This result indicates that the redox charge, i.e., the electrochemical activity, is also related to the property of poly(azure B) itself. Based on the above results, poly(azure B) used in the following experiments was prepared at pH 4.0.

In order to verify whether the doping and dedoping of poly(azure B) would occur during the processes of oxidation and reduction, poly(azure B) film was used for the immobilization of glucose oxidase. Two glucose biosensors were prepared by adsorption and electrochemical doping^[25]. In the latter process, glucose oxidase carrying negative charges was doped into the polymer film during the process of oxidation. Based on the determination of the response current of the biosensors to glucose, the response current of the biosensors formed by doping is larger than that of the biosensor formed by adsorption. This result is in agreement with results from polyaniline glucose biosensors formed by doping and adsorption^[25]. This means that anions in the solution would enter into poly(azure B) film during the oxidation process, and vice versa for the reduction process.

The cyclic voltammetry of azure B in a solution containing 0.5 mol dm^{-3} NaCl and 0.2 mol dm^{-3} with pH 4.0 was carried out in the region of -0.25 to 0.20 V . The result shows that there are an anodic peak at -0.075 V and a cathodic peak at -0.130 V (omitted here), i.e., the separation between the anodic and cathodic peak potentials is 55 mV . The I - E curves for the first to the fifth cycles on the cyclic voltammogram overlap completely. The above results indicate that the redox of azure B at the potential range of -0.25 to 0.20 V is one-electron process and this electrode reaction is reversible. In other words, azure B cannot be polymerized at this potential range. The anodic and cathodic peak potentials of poly(azure B) at pH 4.0 are 0.075 and -0.63 V (curve 3 in Fig. 6), respectively, so the separation between the anodic and cathodic peak potentials is 138 mV . It is clear that the separation between the anodic and cathodic potentials of poly(azure B) is about twice as large as that of azure B. This difference is caused by polymerization, since poly(azure B) consisted of several azure B units.

FTIR Spectrum of Poly(azure B)

The FTIR spectra of azure B and poly(azure B) are shown in Fig. 10, respectively. The FTIR spectrum of azure B is the same as the standard spectrum of azure B presented in Ref. [26]. Both spectra in Fig. 10 are very complicated. For simplicity, we only discuss the main difference between spectrum 1 and spectrum 2. After polymerization, the absorption bands at 3465 , 3394 , 3190 , 1182 and 825 cm^{-1} disappear in spectrum 2; while a broad and intense band at 3408 cm^{-1} appears which becomes more pronounced with respect to the bands at 3040 and 2993 cm^{-1} attributable to stretching vibrations of C—H in aromatic rings and in alkyl —CH₃ groups, respectively; the intensity of the peak at 895 cm^{-1} is much weaker in spectrum 2 than in spectrum 1; and some new small peaks between the wavenumbers 1510 and 1390 cm^{-1} occur in spectrum 2.

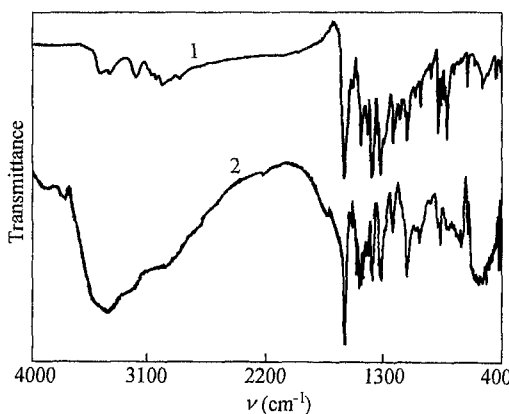
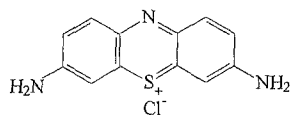
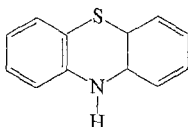


Fig. 10 FTIR spectra of azure B (1) and poly(azure B) (2)

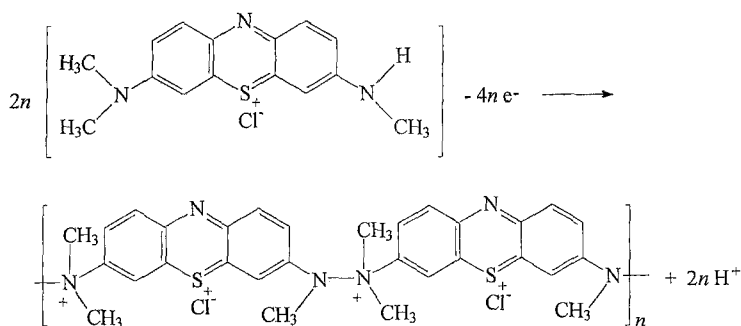
In order to assign the IR bands at 3465, 3394 and 3190 cm^{-1} in spectrum 1, the spectrum of azure B was compared with the Sadtler's standard spectra of methylene blue^[27] and thionine^[28]. The structure of thionine is as follows:



The IR spectrum of methylene blue at wavenumbers higher than 3100 cm^{-1} shows only a broad band between 3400 and 3500 cm^{-1} , which is attributed to a water molecule, indicating the absence of the N—H group in methylene blue. Thus, the peaks at 3465, 3394 and 3190 cm^{-1} in spectrum 1 can only be assigned as the stretching vibrations of N—H of azure B because azure B contains N—H bonds. The IR spectrum of thionine shows two peaks at 3150 and 3330 cm^{-1} , and the intensity of 3150 cm^{-1} is greater than that of 3330 cm^{-1} . Therefore, this confirms that the peak at 3190 cm^{-1} in spectrum 1 is attributed to the N—H stretching vibrations. After polymerization, this peak disappears and a new broad intense band at 3408 cm^{-1} appears in spectrum 2. A possible explanation for the appearance of this band is that the polymerization of azure B was carried out through the connection of N—H bond to form the chain. The new band at 3408 cm^{-1} in spectrum 2 may be attributed to a N—H bond or a O—H bond like that of methylene blue as mentioned above. Since hydrogen bonding involving the N—H hydrogen and O—H hydrogen may cause broadening and shift towards lower wavenumbers, however, the IR spectrum of phenothiazine:



shows a sharp intense peak at 3340 cm^{-1} ^[29]. So perhaps a broad band at 3408 cm^{-1} in spectrum 2 is caused by water like methylene blue. The above results indicate that there is no N—H bond in poly(azure B), thus the polymerization mechanism of azure B is suggested as follows:



We found that phenothiazine under the same conditions as electrolysis of azure B cannot be polymerized. This also implies that the polymerization of azure B is carried out through the connection of N—H bond to form the chain.

As mentioned above, after polymerization, the peaks at 1182 and 825 cm^{-1} attributable to in-plane C—H bending vibration and out-of-plane C—H bending vibration, respectively, disappeared, and the intensity of peak at 825 cm^{-1} reduced considerably in spectrum 2. This indicates that the aromatic C—H bending vibration in azure B is strongly affected by polymerization.

Effect of the Scan Rate on the Cyclic Voltammograms

Figures 11(a) and 11(b) show the effect of the scan rate on the cyclic voltammograms of poly(azure B) in a solution consisting of $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ at pH 3.0 and pH 8.0, respectively. The scan rate (ν) was controlled between 25 and 600 mV s^{-1} . In Fig. 11(a), both the anodic peak potential and cathodic peak potential are independent of scan rate in this scan rate range. This means that poly(azure B) at pH 3.0 has a good electrochemical reversibility and a fast charge transfer characteristic. Based on Fig. 11(a), a plot of anodic peak current (curve 1) and cathodic peak current (curve 2) versus $\nu^{1/2}$ was constructed which shows two straight lines (Fig. 12), indicating that the electrode reaction rate of poly(azure B) was controlled by mass diffusion. Fig. 11(b) shows that the anodic peak potential and cathodic peak potential of the polymer at

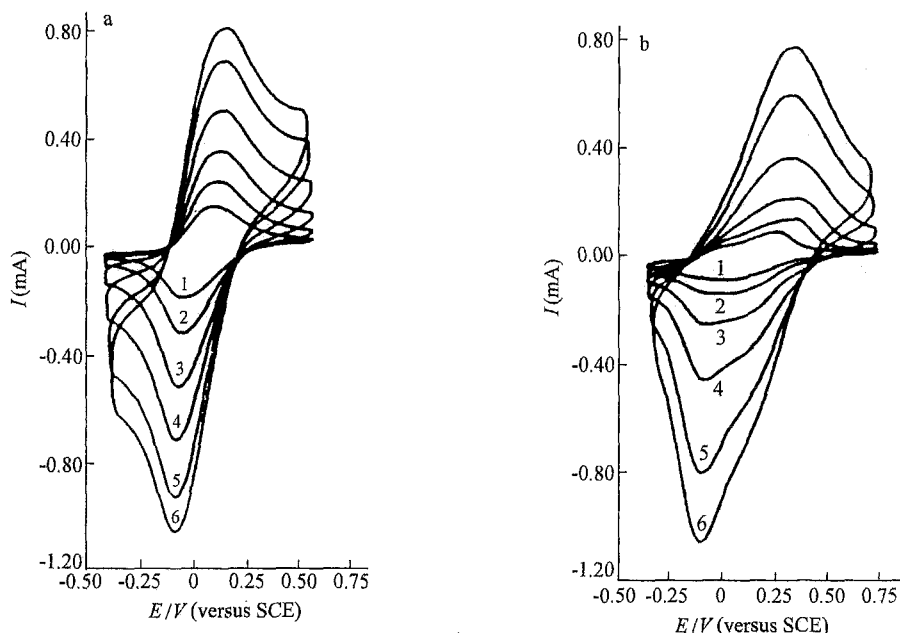


Fig. 11 Effect of the scan rate on the cyclic voltammograms of poly(azure B) in the solution of $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.2 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ with different pH values

a) pH 3.0; b) pH 8.0

Scan rate mV s^{-1} ; Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400, (6) 600

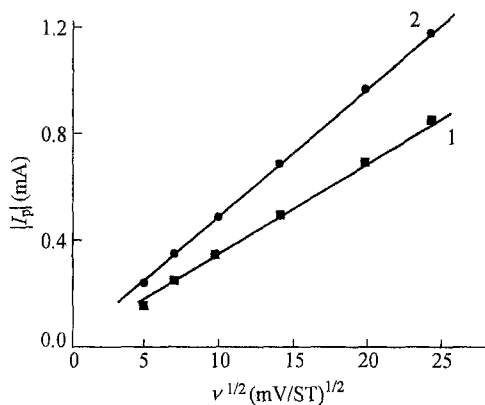


Fig. 12 Plots of anodic peak and cathodic peak currents versus $\nu^{1/2}$, based on the data in Fig. 1

Curves: (1) anodic peak current, (2) cathodic peak current

pH 8.0 shift gradually towards the positive potentials and negative potentials, respectively, with increasing scan rate. This means that the charge transfer in poly(azure B) is affected by pH value, but the electrochemical reaction rate is still controlled by mass transfer at pH 8.0, because there are still an anodic peak and a cathodic peak at the scan rate of 600 mV s^{-1} .

CONCLUSION

A blue poly(azure B) film has been synthesized by the electrochemical polymerization of azure B at various pH values using repeated potential cycling, except at the potentials less than 0.65 V. Poly(azure B) has good electrochemical reversibility, stability and fast charge transfer characteristic in the pH range of 2.0 to 11.0. Anions in the solution can enter into polymer film during the oxidation process, and vice versa in the reduction process. Based on this doping and dedoping characteristic, poly(azure B) can be used for a immobilization of glucose oxidase to form a biosensor. Thus, poly(azure B) could be a good candidate for biomaterials. An electrochemical polymerization mechanism of azure B is proposed in this paper. In fact, the polymerization of azure B and the structure of poly(azure B) are very complicated. Also, the molecular weight and degree of polymerization of poly(azure B) have not been determined in this primary work.

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