Electrochemical Polymerization of Azure A and Properties of Poly(azure A)

Chuanxiang Chen, Shaolin Mu

Department of Chemistry, School of Sciences, Yangzhou University, Yangzhou, 225002, China

ABSTRACT: The electrochemical polymerization of azure A has been carried out using repeated potential cycling. The scan potential is set between -0.2 and 1.3 V (vs. Ag/AgCl). The electrolytic solution consisted of 5 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 with pH 6.0. The temperature for polymerization was controlled at 50°C. An anodic peak and a cathodic peak appear at 0.38 and 0.23 V, respectively, on the cyclic voltammogram of poly(azure A) in 0.5 mol dm^{-3} Na_2SO_4 solution of pH 1.0. Their peak potentials shift toward the negative direction as pH value increases from 1.0 to 4.0. Poly(azure A) has good electrochemical activity and stability in the aqueous solution at the above pH range. The UV-visible spectrum and FTIR spectrum of poly(azure A) are different from those of azure A. The FTIR spectrum of poly(azure A) indicates that no anions were doped into the oxidation form of poly(azure A). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1218–1224, 2003

Key words: azure A; electrochemical polymerization; electrochemical properties; UV-visible spectra; FTIR spectra

INTRODUCTION

After doping, polyacetylene was converted from insulator into conductor.[1] This discovery has revealed a new and vastly important research field for chemists as well as physicists and also plays an important role in looking for synthesis of new materials. Since the discovery of conducting polyacetylene at the end of 1970s, many conducting polymers, such as polyaniline,[2–4] polypyrrole,[5–7] polythiophene,[8,9] and poly(p-phenylene),[10] have been synthesized. For a polymer to be able to conduct electric current, it must consist alternately of single and double bonds between the carbon atoms, and it must also be doped.[11] This is a basic principle for synthesis of new conducting polymers. Conducting polymers and semiconductive polymers have important practical applications in electrode of batteries,[12,13] electrochromic devices,[14] conversion of light to electricity,[15] immobilization of enzymes,[16,17] and light-emitting diodes.[18,19] The various purposes of application need conducting polymers possessed of different properties. Thus, the synthesis of a new type of conducting polymer is very significant. Some of the indicators and dyes have the structure with alternate single and double bonds between the carbon atoms and 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. Therefore, we used repeated potential cycling to study the electrochemical polymerization of a series of indicators and dyes. The advantage for this method is quick to verify whether or not the electrochemical polymerization of a monomer takes place. Among the indicators and dyes under investigation, azure A was found to be polymerized electrochemically.

In fact, Schlereth and Karyakin[20] have reported that azure A can be polymerized electrochemically in the solution consisting of azure A, borax, and $NaNO_3$, since its structure is analogous to those of methylene blue and azure B (Scheme 1).

Methylene blue[21–23] and azure B[24,25] can be polymerized electrochemically. Poly(methylene blue)[22] and poly(azure B)[24] have good electrochemical activity in the pH range of 2–8 and 2–11, respectively, so they can be used for immobilization of enzymes[21,25] and catalysts. However, no study deals with the detailed conditions of the electrochemical polymerization of azure A, film growth, and the electrochemical properties of poly(azure A). In this study, we report the conditions of the electrochemical polymerization of azure A and the electrochemical properties as well as the UV-visible and FTIR spectra of poly(azure A).

EXPERIMENTAL

Azure A and other chemicals used in this work were all of reagent grade. Doubly distilled water was used to prepare solutions. The pH values of the solutions

Azure A   Methylene blue   Azure B
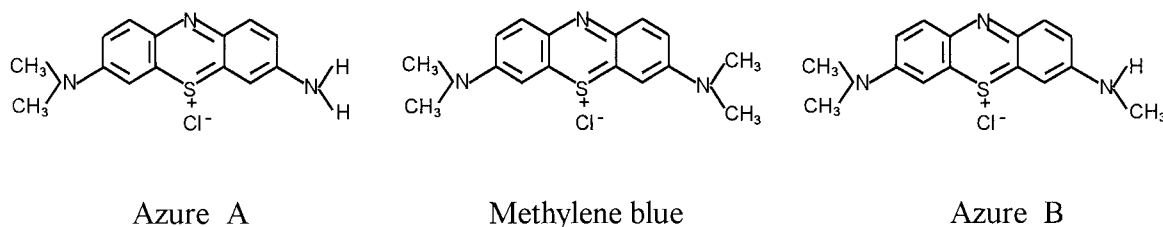
Scheme 1

were determined using PXD-12 meter. The electrolysis cell consisted of two platinum foils and a reference electrode. The area of the working electrode was 4×4 mm^2. Potentials given here are referred to the Ag/AgCl electrode with the saturated KCl solution.

A HPD-1A potentiostat–galvanostat was used for cyclic voltammetry. The scan rate was set at 60 mV s^{-1} for all experiments, except the experiment for the scan rate dependence of cyclic voltammogram. A YEW Model 3036 X-Y recorder was used to record the cyclic voltammograms.

The electrolytic solution consisted of 5 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na$_2$SO$_4$ solution. The pH values of the electrolytic solution used were controlled between 1.0 and 12.0. The electrolysis of azure A was performed using repeated potential cycling at each pH unit interval from the above pH range. The sweeping potential range was set between −0.2 and 1.3 V. The temperature for electrolysis was controlled at 50°C because of the solubility of azure A and the polymerization rate. We found that the polymerization rate of azure A is rather slow at temperature lower than 30°C.

The measurement of the UV-visible spectra of poly(azure A) film polymerized on platinum deposited on quartz glass was carried out using an UV-2501 PC spectrometer. FTIR spectra of azure A and poly(azure A) were measured on pressed pellets with KBr using a Nicolet 740 FTIR spectrometer.

RESULTS AND DISCUSSION

Electrochemical polymerization of azure A

Figure 1 shows the cyclic voltammograms during electrolysis of azure A solution with pH 1.0. There are two anodic peaks at 0.25 and 0.45 V and two cathodic peaks at 0.14 and 0.41 V for the first cycle (curve 1) and second cycle (curve 2). The anodic current increases quickly beginning at 1 V, and a shoulder peak occurs at 1.2 V. As the electrolysis proceeds, an anodic peak and a cathodic peak occur at 0.35 and 0.15 V for the 10th cycle, respectively. Their peak currents are much higher at the 10th cycle than at the 1st cycle. After electrolysis, a deep-blue film was formed on the working electrode, which is poly(azure A).

Figure 2 shows the cyclic voltammograms for the electrolysis of the above solution, but with a pH of 6.0.

The cyclic voltammograms in Figure 2 are similar in shapes to those in Figure 1. The difference between Figures 1 and 2 is that a prominently anodic peak appears at 1.08 V on curve 1 in Figure 2 for the first cycle. Two anodic peaks shift to 0.03 and 0.31 V, two cathodic peaks shift to −0.10 and 0.23 V on curve 1 in Figure 2. It is clear that the shift of the peak potentials is caused by the pH value of the electrolytic solution, which affects the redox potential of azure A. The currents of the anodic and cathodic peaks increase first from the 1st cycle to the 10th cycle, and then decrease slowly from the 10th cycle to the 20th cycle. This is caused by the film conductivity. After electrolysis, a deep-blue film was found in the working electrode.

To prove the attribution of the two pairs of redox peaks at a lower potential range, a separate experiment for the electrolysis of the same solution was performed between −0.20 and 0.50 V. The result is shown in the inset in Figure 2. It is clear that there are also two anodic peaks at 0.03 and 0.31 V, and two
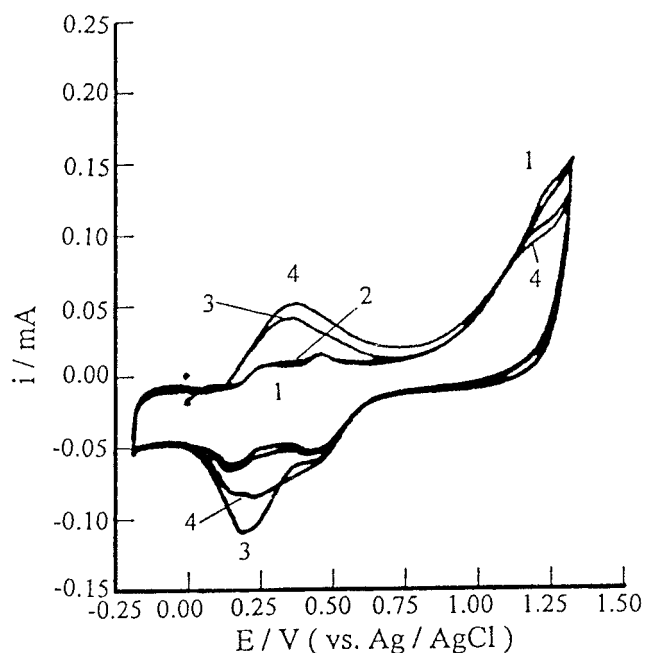

Figure 1 Cyclic voltammograms for electrolysis of the solution consisting of 5 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na$_2$SO$_4$ with pH 1.0. Curves: (1) 1st cycle, (2) 2nd cycle, (3) 10th cycle, (4) 20th cycle.
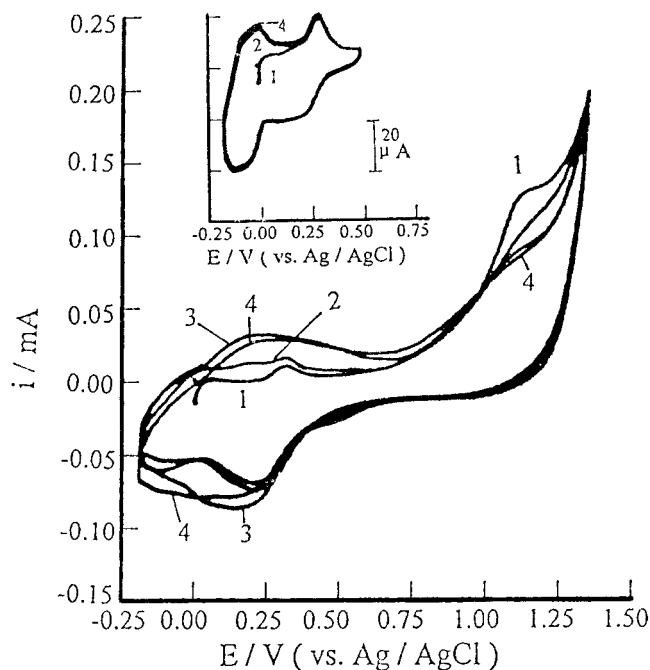
Figure 2 Cyclic voltammograms for electrolysis of the solution consisting of 5 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na$_2$SO$_4$ with pH 6.0. Curves: (1) 1st cycle, (2) 2nd cycle, (3) 10th cycle, (4) 20th cycle.

cathodic peaks at -0.10 and 0.23 V. Their peak potentials and peak currents are almost independent of the number of potential cycles. Thus, the two pairs of redox peaks on curve 1 in Figure 2 in the lower potential range are caused by the redox of azure A itself.

Figure 3 shows the cyclic voltammograms for the electrolysis of the same solution as shown in Figure 1, but with a pH of 12.0. Its cyclic voltammograms are much different in shapes from those in Figures 1 and 2. This is caused by pH value of the electrolytic solution. But after electrolysis, a deep-blue film was also formed on the working electrode.

Figure 4 is the cyclic voltammograms of poly(azure A) films in 0.5 mol dm^{-3} Na$_2$SO$_4$ solution of pH 1.0. The 12 pieces of poly(azure A) films were synthesized under each pH value in pH range of 1.0 to 12.0, which is correspondent with the number of curves in Figure 4. Each piece of poly(azure A) film used in this experiment was obtained using repeated potential cycling for 20 cycles. From Figure 4 we can see that the cathodic peak potential of poly(azure A) is affected by the pH value of the electrolytic solution for preparing poly(azure A). And from the areas of cyclic voltammograms, the electrochemical activity of poly(azure A) prepared at pH 6.0 (curve 6), that is, the redox charge of poly(azure A), is the largest among the samples. Therefore, poly(azure A) used following experiments was prepared in the above electrolytic solution of pH 6.0.

Recently, we found that azure A also can be polymerized in the solution of pH <1. pH range for poly-

merization of methylene blue,[22] azure B,[24] and azure A are 6.0 to 12.0, 2.0 to 11.0, and <1 to 12.0. It is clear that this difference is related to their molecular structure. The pH range for polymerization of this kind of compounds decreases with increasing number of H in the group of (CH$_3$)$_2$N—.

Electrochemical properties of poly(azure A)

Curves 1–4 in Figure 5 are the cyclic voltammograms of poly(azure A) in 0.5 mol dm^{-3} Na$_2$SO$_4$ solutions with pH 1.0, 2.0, 3.0, and 4.0, respectively. An anodic peak and a cathodic peak appear at 0.38 and at 0.23 V, respectively, on curve 1. Their peak potentials shift toward more negative potentials with increasing pH value. This indicates that the redox of poly(azure A) is related to the concentration of protons. This behavior is similar to that of polyaniline.[26] Their peak currents decrease a little with increasing pH value, that is, the electrochemical activity of poly(azure A) is slightly affected by pH value in the pH range of 1.0–4.0. This property is much different from that of polyaniline.[26]

Poly(methylene blue) has an electrochemical activity in the pH range of 2.0–8.0,[22] and poly(azure B) has an electrochemical activity in the pH range of 2.0–11.0.[24] It is clear that the pH range of poly(azure A) for its electrochemical activity decreases compared with poly(methylene blue) and poly(azure B). This is also related to the structure of the monomers as mentioned above.
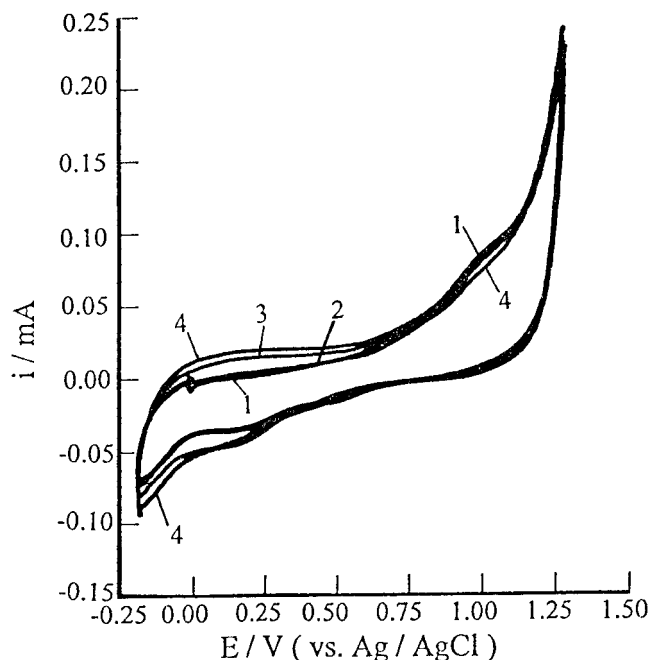

Figure 3 Cyclic voltammograms for electrolysis of the solution consisting of 5 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na$_2$SO$_4$ with pH 12.0. Curves: (1) 1st cycle, (2) 2nd cycle, (3) 10th cycle, (4) 20th cycle.
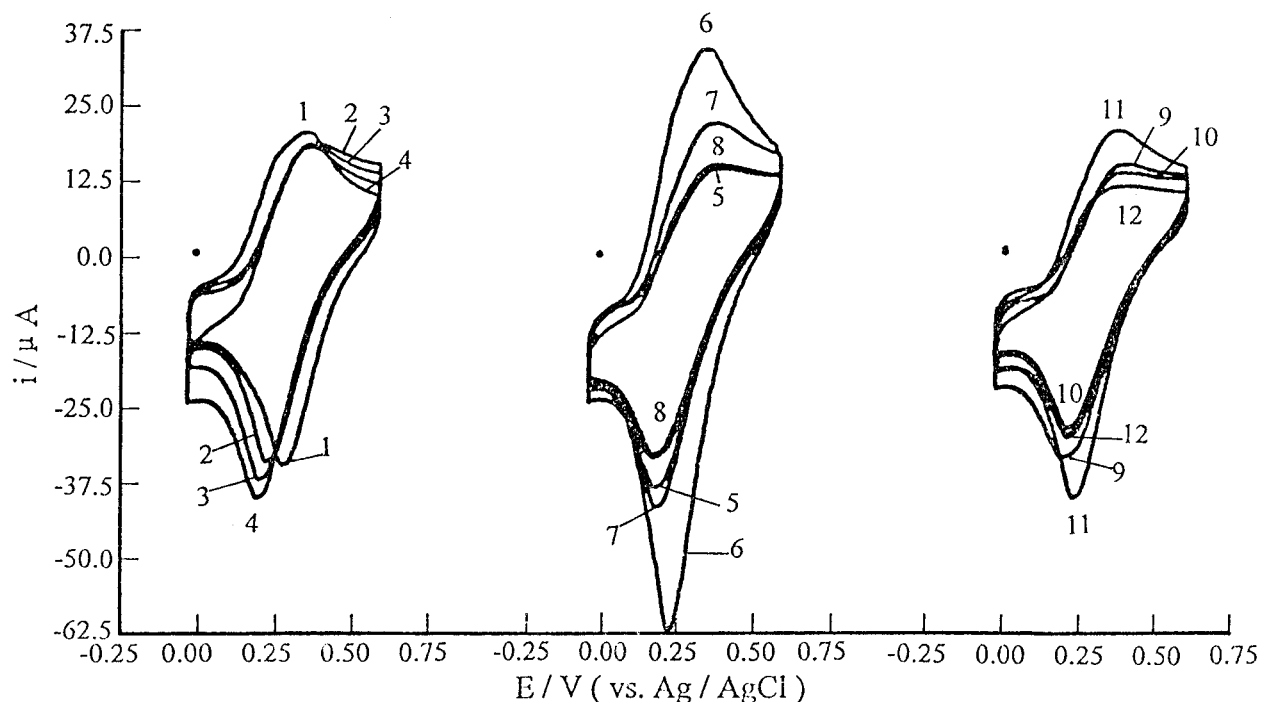
Figure 4 Cyclic voltammograms of poly(azure A) films in 0.5 mol dm^{-3} Na$_2$SO$_4$ solution of pH 1.0. The films were synthesized at different pH values. The number of curves in plots is corresponding to pH value of the electrolytic solution.

Figure 6(a,b) shows the effect of the potential scan rate on the cyclic voltammograms of poly(azure A) in 0.5 mol dm^{-3} solution with pH 1.0 and 3.0, respectively. Their peak currents in both plots increase with increasing scan rate, and both anodic peak and cathodic peak potentials shift slightly toward the more positive and negative potentials, respectively, as the scan rate increases from 25 to 600 mV s^{-1}. This may be caused by low conductivity of poly(azure A).

In both plots, there are still a sharp anodic peak and a sharp cathodic peak at 600 mV s^{-1}. This indicates

that the electrochemical reaction is still controlled by mass transfer at such a high scan rate.

Based on the relationship between the scan rate v and anodic peak current, both plots of i_{pa} versus $v^{1/2}$
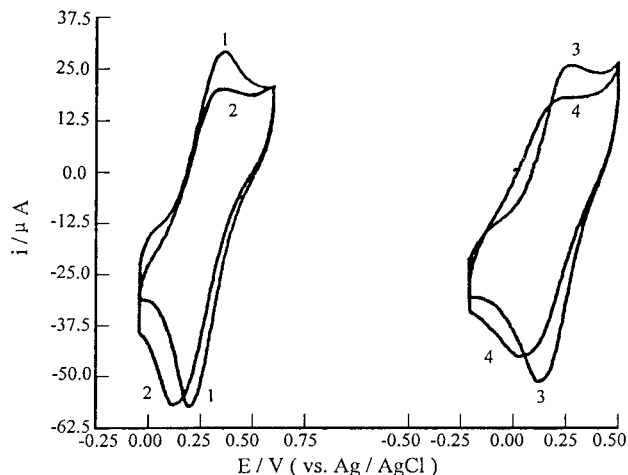

Figure 5 Effect of pH value on the cyclic voltammograms of poly(azure A) in 0.5 mol dm^{-3} Na$_2$SO$_4$ solution. Curves: (1) pH 1.0, (2) pH 2.0, (3) pH 3.0, (4) pH 4.0.
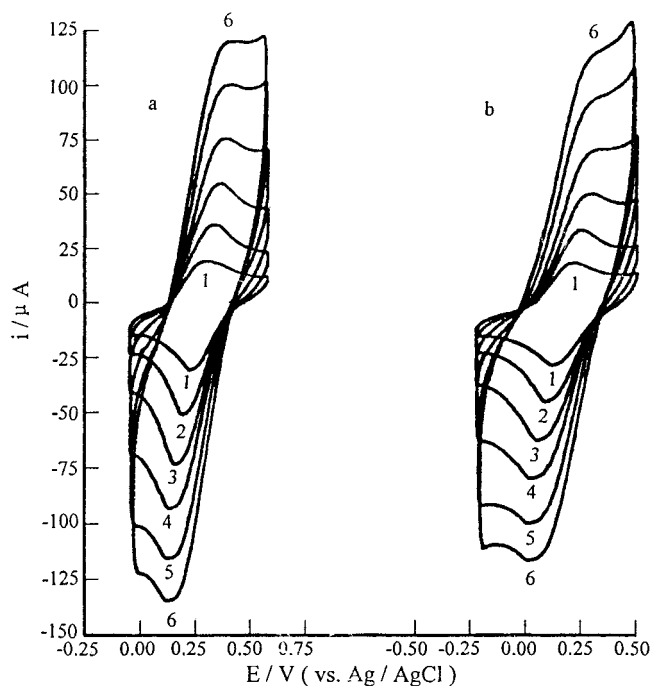

Figure 6 Effect of potential scan rate on the cyclic voltammograms of poly(azure A) in 0.5 mol dm^{-3} Na$_2$SO$_4$ solution: (a) pH 1.0, (b) pH 3.0. Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400, (6) 600 mV s^{-1}.
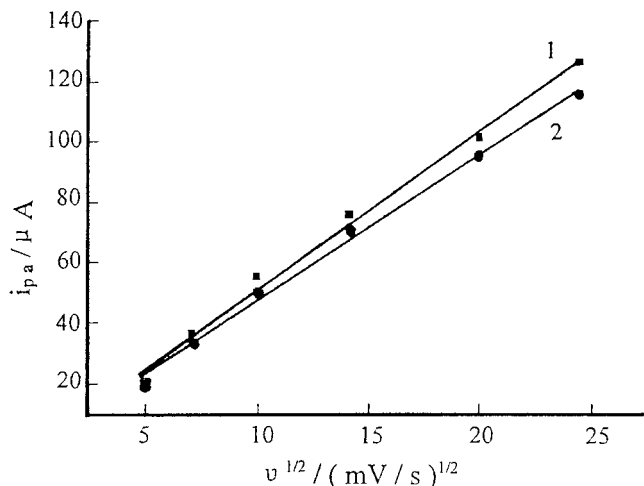
Figure 7 Plot for i_{pa} versus $v^{1/2}$, Curves: (1) pH 1.0, (2) pH 3.0. Based on the data shown in Figure 6

are all straight lines (Fig. 7). Lines 1 and 2 represent the experimental results obtained from the solutions of pH 1.0 and 3.0 (Fig. 6), respectively. This again identifies that the electrode reaction of poly(azure A) is controlled by mass transfer and poly(azure A) still has a good ability of the charge transfer at pH 3.0.

Figure 8(a,b) shows the cyclic voltammograms of poly(azure A) in 0.5 mol dm^{-3} Na$_2$SO$_4$ solutions of pH 1.0 and 4.0, respectively. Curves 1 and 2 in both plots are the first and fiftieth cycles. It is clear that the i–E curves of the first and fiftieth cycles are almost overlapped. Thus, poly(azure A) has good stability in the aqueous solution.

UV-visible spectra

Curves 1 and 2 in Figure 9 show the UV-visible spectra of the solution containing azure A and 0.5 mol dm^{-3}
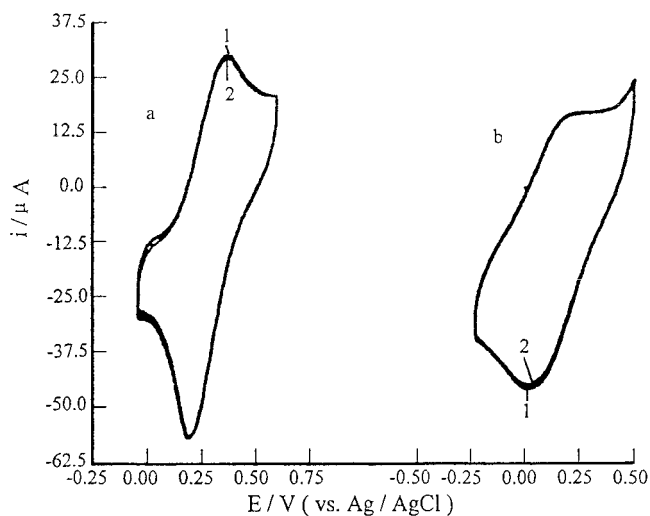

Figure 8 Stability of poly(azure A) in 0.5 mol dm^{-3} Na$_2$SO$_4$: (a) pH 1.0, (b) pH 4.0. Curves: (1) 1st cycle, (2) 50th cycle.
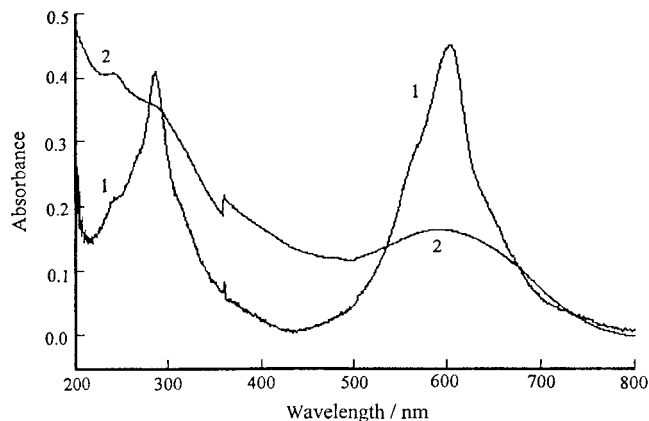
Figure 9 UV-visible spectra. Curves: (1) azure A in 0.5 mol dm^{-3} Na$_2$SO$_4$ with pH 6.0, (2) poly(azure A).

Na$_2$SO$_4$ with pH 6.0 and poly(azure A) film, respectively. There are two absorption peaks at 285 and 602 nm on curve 1. After polymerization, the sharp peak at 285 nm almost disappears on curve 2; only a broad band at 600 nm remains on curve 2. The difference between two spectrum lines indicates that azure A was polymerized.

Also, a pronounced peak around 290 nm occurs in UV-visible spectra of methylene blue in 0.5 mol dm^{-3} sodium tetraborate and 0.5 mol dm^{-3} KCl with pH 9.19[22] and in 0.05 mol dm^{-3} phosphate buffer with pH 7.5.[23] After polymerization, this peak becomes very small.[22] So the change in the UV-visible spectra of azure A before and after polymerization is very similar to that of methylene blue. This is because the structure of azure A is analogous to that of methylene blue.

FTIR spectra

Table I shows the wave number of absorption peaks for the FTIR spectra of azure A and poly(azure A). The FTIR spectrum of poly(azure A) synthesized here is different from that synthesized electrochemically in

TABLE I
Wave Number (cm^{-1}) of FTIR Spectra for Azure A and Poly(azure A)

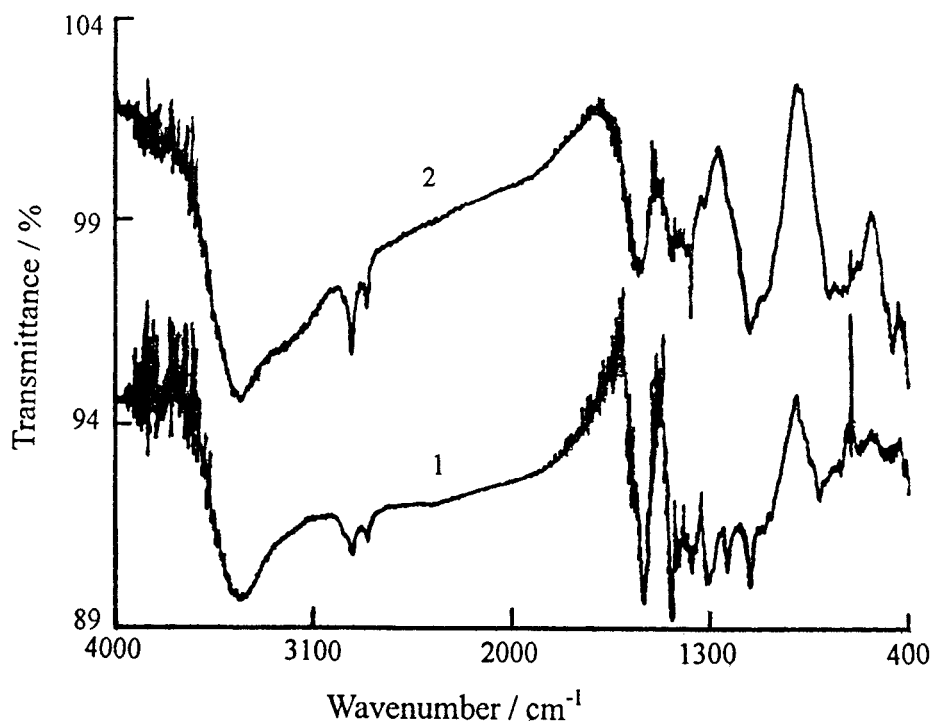| Azure A	Poly(azure A)
3,429 (s)	3,436 (s)
2,922 (m)	2,922 (m)
2,852 (m)	2,852 (m)
1,591 (s)	1,619 (m)
1,471 (s)	1,480 (m)
1,379 (s)	1,386 (s)
1,309 (s)	
1,224 (s)	
1,126 (s)	1,126 (s)
809 (m)	
767 (w)	767 (m)

Figure 10   FTIR spectra. Spectrum lines: (1) azure A, (2) poly(azure A).

the solution containing azure A, borax, and sodium nitrate with pH 9.1,[20] in which a peak at 1,603 cm^{-1} is the strongest relative to other peaks and the peaks at 1,329 (m) and 1,231 (w) cm^{-1} occur in IR spectrum of poly(azure A). However, the relative intensity of the peak at 1,619 cm^{-1} is not the strongest among all peaks (curve 2 in Fig. 10), and no peaks at 1,329 and 1,231 cm^{-1} occur in the FTIR spectrum of poly(azure A) synthesized here.

The spectrum lines 1 and 2 in Figure 10 show the FTIR spectra of azure A and poly(azure A), respectively. The peak at 3,429 cm^{-1} on spectrum 1 is attributed to the stretching vibration of N—H in —NH$_2$ group of azure A. The peaks at 2,922 and 2,852 cm^{-1} on spectrum 1 are attributed the asymmetrical and symmetrical vibrations of C—H bonds in two —CH$_3$ groups. Comparison of spectrums 2 and 1 shows that no changes are observed between the two spectrum lines at wave number greater than 2,000 cm^{-1}. This indicates that the —NH$_2$ and —CH$_3$ groups of azure A were not changed after polymerization.

The peaks at 1,591 and 1,471 cm^{-1} on spectrum 1 are attributed to the stretching vibrations of C=C in aromatic rings. They also occur on spectrum 2, but their peak positions shift to 1,619 and 1,480 cm^{-1}, respectively. The peak at 1,379 cm^{-1} (s) on spectrum 1 is attributed to the asymmetric CH$_3$ bending vibration in dimethyl groups.[27] This peak also occurs on spectrum 2; only its position shifts to 1,386 cm^{-1} (s). This again proves that —CH$_3$ groups was not altered after polymerization. Two peaks at 1,309 (s) and 1,224 cm^{-1}

attributable to in-plane C—H bending vibrations for aromatic rings[28] occur on spectrum 1, and the peak at 809 cm^{-1} attributable to out-of-plane C—H bending vibration for aromatic rings[28] occurs on spectrum 1. However, these three peaks almost disappear on spectrum 2. This indicates that the aromatic C—H bending vibration in azure A is strongly affected by polymerization, which is similar to that of azure B.[24] Since the structure of azure A is analogous to that of azure B. It is clear that the IR absorption peak number of poly(azure A) is less than that of azure A. This is a characteristic of polymerization of a monomer.

The above FTIR spectra provide a piece of information that only the vibration models of aromatic rings were changed after polymerization. So we assume that the polymerization of azure A is carried out through the coupling of aromatic rings to form the chain.

The question for the FTIR spectrum of poly(azure A) is that there is no absorption peak of SO$_4^{2-}$ ions on spectrum 2. This peak should occur at 1,080–1,130 cm^{-1} on IR spectrum of poly(azure A). Because the polymerization of azure A was carried out in the solution of Na$_2$SO$_4$, the anion SO$_4^{2-}$ should be doped into poly(azure A) during the polymerization process of azure A. The IR spectrum of polyaniline at the oxidation form has a very strong absorption peak of doped cations, such as BF$_4^-$ and NO$_3^-$ ions.[29] However, no absorption peak of SO$_4^{2-}$ ions occurs on spectrum 2. This indicates that SO$_4^{2-}$ ions were not doped into poly(azure A). For a conducting polymer, it must be doped as mentioned previously. This gives us the

information that the conductivity of poly(azure A) should be low. The conductivity of poly(azure A) was measured using a four-probe technique to be 2.1×10^{-6} S cm^{-1}. So its conductivity is really very low. The relationship between the conductivity and IR spectrum of poly(azure A) confirms a basic principle for preparing a conducting polymer that doping is a necessary condition for the conducting polymer.

CONCLUSIONS

A blue poly(azure A) film has been synthesized by the electrochemical polymerization of azure A. However, the pH value for polymerization of azure A is lower than those of methylene blue and azure B. This is related to their molecular structures. The polymerization rate of azure A and the electrochemical properties of poly(azure A) are affected by the pH value of the electrolytic solution and temperature. Poly(azure A) has good electrochemical activity and stability in the pH range of 1.0–4.0. This pH range is also smaller than those of poly(methylene blue) and poly(azure B). This is also caused by the structure of the monomers. Based on the FTIR spectra of azure A and poly(azure A), a polymerization mechanism of azure A is presented in the article, but it is only an assumption.

References

1. Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. J Am Chem Soc 1978, 100, 7729.
2. Bacon, J.; Adams, R. N. J Am Chem Soc 1968, 90, 6596.
3. MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W. G.; Yaniger, S. I. Mol Cryst Liq Cryst 1985, 121, 173.
4. Geniès, E. M.; Lapkowski, M. J Electroanal Chem 1987, 236, 189.
5. Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. J Chem Soc Chem Commun 1979, 14, 635.
6. Geniès, E. M.; Bidan, G.; Diaz A. F. J Electroanal Chem 1983, 149, 101.
7. Pei, Q.; Qian, R. Synth Met 1991, 45, 35.
8. Tourillon, G.; Garnier, F. J Electroanal Chem 1982, 135, 173.
9. Tanaka, K.; Shichiri, T.; Yamabe, T. Synth Met 1986, 16, 207.
10. Speight, J. G.; Kovacic, P.; Koch, F. W. J Macrol Sci 1971, 5, 295.
11. Epstein, A. J. Synth Met 2001, 116, 7.
12. Wang, B. C.; Li, C. Z.; Wang, F. S. J Power Sources 1988, 24, 115.
13. Kan, J. Q.; Xue, H. G.; Mu, S. L. J Power Sources 1998, 74, 113.
14. Kobayashi, T.; Yoneyama, N.; Tamura, H. J Electroanal Chem 1984, 177, 281.
15. Dong, Y. H.; Mu, S. L. Electrochim Acta 1991, 36, 2015.
16. Bartlett, P. N.; Whitaker, R. G. Biosensors 1987, 3, 359.
17. Mu, S. L.; Xue, H. G.; Qian, B. D. J Electroanal Chem 1991, 304, 7.
18. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Nature 1990, 347, 539.
19. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789.
20. Schlereth, D. D.; Karyakin, A. A. J Electroanal Chem 1995, 395, 221.
21. Karyakin, A. A.; Strakhova, A. K.; Karyakina, E. E.; Varfolomeyev, S. D. Bioelectrochem Bioenerg 1993, 32, 35.
22. Liu, J. C.; Mu, S. L. Synth Met 1999, 107, 159.
23. Karyakin, A. A.; Karyakina, E. E.; Schmidt, H. L. Electroanalysis 1999, 11, 149.
24. Shan, D.; Mu, S. L. Chin J Polym Sci 2001, 19, 359.
25. Shan, D.; Mu, S. L. Electroanalysis 2001, 13, 493.
26. Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. J Chem Soc Faraday Trans 1986, 82, 2385.
27. Nakanishi, K.; Solomon, P. H. Infrared Absorption Spectroscopy, 2nd edn.; Holden-Day: San Francisco, 1977; p 16.
28. Gilbert, B. C. Investigation of Molecular Structure; Bell and Hyman: London, 1984; p 62.
29. Mu, S. L.; Kan, J. Q. Synth Met 1998, 98, 51.