Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Chen, Chuanxiang and Gao, Yuhua(2007) 'Electrosynthesis of Poly(azure B) from Sulfuric Acid Solution', Journal of Macromolecular Science, Part A, 44: 10, 1089 — 1093
To link to this Article: DOI: 10.1080/10601320701521589
URL: http://dx.doi.org/10.1080/10601320701521589

Journal of Macromolecular Science®*, Part A: Pure and Applied Chemistry* (2007) **44**, 1089–1093

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701521589

Electrosynthesis of Poly(azure B) from Sulfuric Acid Solution

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Received February, 2007, Accepted March, 2007

Electrochemical polymerization of azure B from sulfuric acid solution was carried out by using cyclic voltammetry. The electrolytic solution consisted of 5.0 $\text{mmol} \cdot \text{dm}^{-3}$ azure B and 0.3 $\text{mol} \cdot \text{dm}^{-3}$ H_2SO_4. The temperature for polymerization was controlled at 20°C. A blue film, i.e., poly(azure B) was formed on a platinum foil and had a electrochemical reversibility, stability and a fast charge transfer ability in the 0.5 $\text{mol} \cdot \text{dm}^{-3}$ Na_2SO_4 with pH ≤ 4.0 solution. The currents of both anodic and cathodic peaks are proportional to $\upsilon^{1/2}$ at the scan rate (υ) region of 25 and 600 $\text{mV} \cdot \text{s}^{-1}$ on the cyclic voltammograms. The conductivity of poly(azure B) is $2.8 \times 10^{-6}\ \text{S} \cdot \text{cm}^{-1}$ at 20°C. The UV-visible spectrum and Raman spectrum of the polymer are different from those of the monomer. A possible polymerization mechanism of azure B was also proposed.

Keywords: conducting polymer; electrochemistry and cyclic voltammetry

1 Introduction

Conducting polymers have been widely studied because of their potential use as battery electrodes, electrochromic devices, light-emitting diodes and immobilization of enzymes (1). In general, conducting polymer materials based on conjugated polymers function as conductors of electricity due to electron delocalization through their planar π-system (2). Due to the conjugative parent ring structure, interest in conjugated polymers that contain azine ring backbones has been sparked by the promise of a new class of conducting polymers (3, 4). In fact, Shan et al. (5−9) have reported the monopolymerization of azure B, an azine derivative, from weak acidic, neutral and basic aqueous solutions and copolymerization of azure B and aniline in neutral aqueous media. They investigated the fact that poly(azure B) can been used for immobilization of an enzyme (5, 8, 9) and that the conductivity of the copolymer synthesized is four orders of magnitude higher than that of polyaniline synthesized under the same conditions, but in the absence of azure B (7). Sha et al. (10) reported that the electropolymerization of azure B on screen-printed carbon electrodes took place in neutral phosphate buffer and the poly(azure B) modified electrodes exhibited electrocatalysis and stability for NADH oxidation. Recently, Huang et al. (11) studied the electrochemical behavior of glucose on a poly(azure B)/copper nanocomposite film modified glassy carbon electrode. They also synthesized poly(azue B) from a neutral aqueous solution (11).

However, it is known that the electropolymerization from acidic solutions is generally preferable for formation of an electroactive polymer (3) and the regular polymer growth in cyclic voltammetric conditions with a limited anodic switching potential requires acidic solutions (12). Taking into account that electropolymerization of either thionine or neutral red from acidic solutions has been reported (13−17) and that the structure of azure B is similar to those of thionine and neutral red (3), we believe that azure B may be electropolymerized in acidic media. Surprisingly, to date, there have been few studies concerning the polymerization reaction of azure B in strongly acidic solutions, and the structure of poly(azure B) has not yet been studied in detail (3, 18). In the present article we present an electrochemical polymerization reaction of azure B on a platinum anode in aqueous sulfuric acid solution, the electrochemical properties, UV-visible spectrum, Raman spectrum and possible chemical structure of poly(azure B).

2 Experimental

2.1 Reagents

The chemicals used were all reagent grade. Doubly distilled water was used to prepare solutions.

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2.2 Electropolymerization

An electrolytic solution is usually a mixture of a solvent (here water) and an electrolyte (here H_2SO_4 or Na_2SO_4). The electroactive azure B was added into the solution to prepare a polymer. The electrolysis of azure B was carried out using repeated potential cycling in the solution consisting of 5.0 $mmol \cdot dm^{-3}$ azure B and 0.3 $mol \cdot dm^{-3}$ H_2SO_4.

We used cyclic voltammetry to study the electropolymerization of azure B. The scan rate was 50 $mV \cdot s^{-1}$. The sweeping potential ranges were set in the region of 0 and 1.10 V, and 0 and 0.50 V, respectively. The electrochemical experiments were carried out at 20°C.

2.3 Equipment and Measurements

The pH values of solutions were determined using a PXD-12 meter. The electrolysis cell consisted of two platinum foils and a SCE reference electrode (all potentials are given against this reference). The area of the platinum foil was $3 \times 3\ mm^2$.

A HPD-1A potentiostat-galvanostat was used for the cyclic voltammetry. The scan rate was set at 50 $mV \cdot s^{-1}$ for all experiments, except for the experiments for the scan rate dependence of cyclic voltammogram. A YEW Model 3086 X-Y recorder was used to record the cyclic voltammograms.

To measure the electrochemical properties of the poly (azure B) films, an electrolytic solution is prepared by mixing a solvent (here water) and an electrolyte (here Na_2SO_4).

The measurement of the UV-visible spectrum of poly (azure B) film polymerized on platinum deposited on quartz glass was carried out by using an UV-2501 PC spectrometer. Raman spectra of azure B and poly (azure B) were measured by using a Lab Ram I confocal microspectrometer.

The conductivity of poly(azure B) was measured on a pressed pellet by using a four-probe technique.

3 Results and Discussion

3.1 Electrochemical Polymerization of Azure B

Figure 1(a) shows the cyclic voltammograms for electrolysis of azure B under the experiment conditions as described in the Figure 1 caption. There is an anodic peak at 0.20 V and a cathodic peak at 0.18 V for the first cycle (curve 1). The anodic current increases quickly beginning at 0.88 V, and a peak appears at 1.05 V for the first cycle (curve 1), and then the anodic peak current decreases quickly for the second cycle (curve 2). However, the anodic peak current decreases slowly from the tenth cycle (curve 3) afterwards. This is mainly caused by the low conductivity of poly(azure B), since azure B was polymerized on the polymer film in this case. As a result, the anodic peak current changes little.

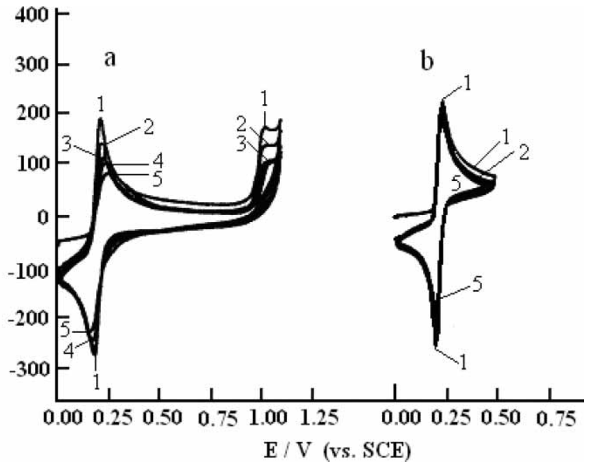

Fig. 1. Cyclic voltammograms of polymerization of azure B during electrolysis of the solution consisting of 5.0 $mmol \cdot dm^{-3}$ azure B and 0.3 $mol \cdot dm^{-3}$ H_2SO_4, at a scan rate of 50 mV/s, at 20°C, potential range of (a) 0 and 1.10 V and (b) 0 and 0.5 V. Curves: (1) first cycle, (2) second cycle, (3) 10th cycle, (4) 20th cycle, (5) 30th cycle.

The currents of a pair of redox peaks about 0.20 V decrease quickly with an increasing number of potential cycles. In addition, the anodic peak potential shifts toward more positive values with an increasing number of potential cycles, while the corresponding cathodic peak potential shifts toward more negative values during the electrolysis. The above results indicate that the polymer film grows with time. Indeed, a blue film, i.e., poly(azure B) was found on the working electrode after the electrolysis.

To prove the attribution of the pair of redox peaks at a lower potential range, a separate experiment for electrolysis of the same solution was performed between 0 and 0.5 V. The result is shown in Figure 1(b). It is clear that there is an anodic peak at 0.20 V and a cathodic peak at 0.18 V. The peak potentials and peak currents are almost independent of potential cycles. After electrolysis, no polymer film was formed in this potential region, only a pair of electrochemical redox peaks of azure B took place in the potential range between 0 and 0.50 V, which is very similar to those of neutral red and thionine themselves in aqueous solutions of an acid (13, 14). Thus, the pair of redox peaks on curve 1 in Figure 1(a) in the lower potential range are caused by the redox of azure B itself. This conclusion is in agreement with previous literature (5).

The conductivity of poly(azure B) was measured on a pressed pellet, which is $2.8 \times 10^{-6}\ S \cdot cm^{-1}$ at 20°C.

3.2 Electrochemical Properties of Poly(azure B)

The electrochemical activities of polymer films were examined using cyclic voltammetry. Poly(azure B) used in the following experiments was obtained by using repeated potential cycling at the potential range of 0 and 1.10 V for 20 cycles.

Figure 2 shows the cyclic voltammograms of poly(azure B) in the solution of 0.5 $mol\ dm^{-3}$ Na_2SO_4 with various pH values. In the solution of pH 1.0, there is an anodic peak at

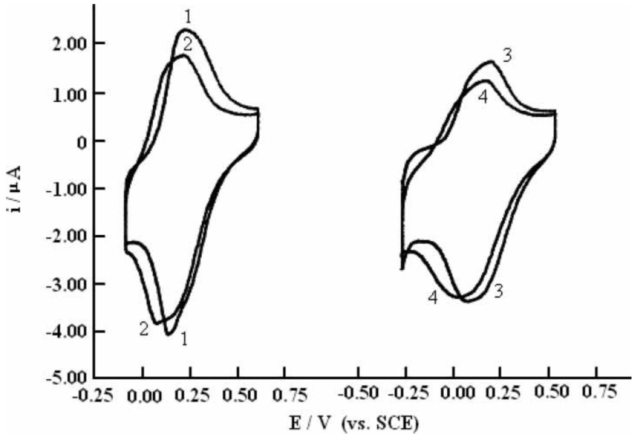

Fig. 2. Effect of pH value on the cyclic voltammograms of poly(-azure B) in 0.5 mol · dm^{-3} Na_2SO_4 solution. Curves: (1) pH 1.0, (2) pH 2.0, (3) pH 3.0, (4) pH 4.0.

0.24 V and a corresponding cathodic peak at 0.13 V on curve 1. The potentials of both peaks shift toward more negative potentials with increasing pH values from 2.0 to 4.0. This means that the redox processes of poly(azure B) are related to the proton concentration, i.e., protons enter into the solution from the polymer during the oxidation process, and vice versa for the reduction process. This poly (azure B) behavior is similar to that of polyaniline (19). However, their peak currents decrease a little with increasing pH value, i.e., the electrochemical activity of poly(azure B) is slightly affected by pH value in the 1.0 to 4.0 pH range, which is much different from that of polyaniline (19).

After recording the cyclic voltammogram of each of poly (azure B) in the solution of pH 4.0, the polymer film was put into the solution of pH 1.0, the cyclic voltammogram was recorded again. Its *i-E* curve on the cyclic voltammogram is almost the same as curve 1 in Figure 2. Moreover, the cyclic voltammograms of poly(azure B) in 0.5 mol · dm^{-3} Na_2SO_4 solutions of pH 1.0 and 4.0 were recorded for 50 cycles, respectively. The *i-E* curves (not shown here) of the first and 50th cycles almost overlapped. Thus, poly(azure B) has good stability in aqueous solution. This means that each poly(azure B) has a good electrochemical reversibility and stability at the 1.0 to 4.0 pH range.

Figures 3(a) and (b) shows the effect of the potential scan rate on the cyclic voltammograms of poly (azure B) in 0.5 mol · dm^{-3} Na_2SO_4 solution with pH 1.0 and 4.0, respectively. Their peak currents in both plots increase with increasing scan rate, and the both anodic peak and cathodic peak potentials shift slightly towards the more positive and negative values, respectively, as the scan rate increases from 25 to 600 mV s^{-1}. This may be caused by low conductivity of poly(azure B).

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.

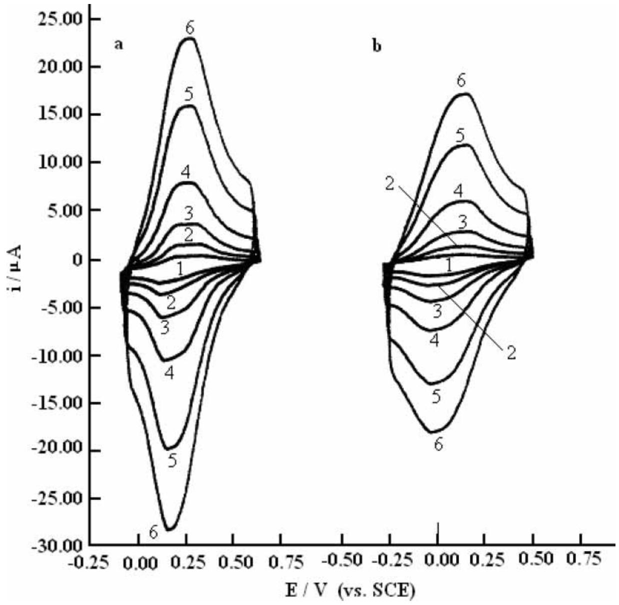

Fig. 3. Effect of potential scan rate on the cyclic voltammograms of poly(azure B) in 0.5 mol · dm^{-3} Na_2SO_4 solutions, (a) pH 1.0, (b) pH 4.0. Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400, (6) 600 mV s^{-1}.

Based on the relationship between the scan rate υ and the anodic (cathodic) peak current, both plots of cathodic peak current i_{pa} (i_{pc}) vs. $\upsilon^{1/2}$ are all straight lines (not shown here). This again shows that the electrode reaction of poly (azure B) is controlled by mass transfer and poly(azure B) still has a good ability of the charge transfer at pH 4.0.

3.3 UV-Visible Spectra

Curves 1 and 2 in Figure 4 show the UV-visible spectra of azure B in 0.3 mol dm^{-3} H_2SO_4 and poly(azure B) synthesized on platinum deposited on quartz glass at the potential range of 0 and 1.10 V using a sweeping potential method,

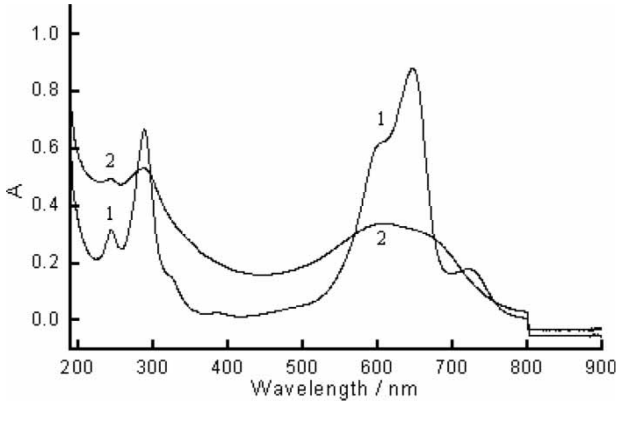

Fig. 4. UV-visible spectra for azure B and poly(azure B). Curves: (1) azure B solution, (2) poly(azure B) polymerized on platinum deposited on quartz glass using cyclic voltammetry at the potential range of 0 and 1.10 V.

respectively. There are seven peaks at 244.5, 289.5, 328.0 (shoulder), 382.0 (very weak), 603.0 (shoulder), 647.0 and 721.0 nm on curve 1 for the azure B solution and four peaks at 243.5, 287.5, 605.5 and 674.5 nm (shoulder) on curve 2 for the poly(azure B) film. One main difference between curve 1 and curve 2 is that the three peaks about 328.0, 382.0 and 721.0 nm disappear in curve 2. One difference is that the wavelength of the peak at 647.5 nm (in curve 1) shifts longer about 27 nm, which means the chain of the polymer is longer than the monomer azure B. Another difference is that the absorbance of the 647.5 nm peak decreases so markedly that the peak becomes a shoulder one of the peak at 605.5 nm (in curve 2). The change in the UV-visible spectra of azure B before and after polymerization is very similar to that of methylene blue (20). This is because the structure of azure B is analogous to that of methylene blue. So the differences between two spectrum lines indicate that azure B was polymerized.

3.4 *Ramam Spectra*

The spectrum lines 1 and 2 in Figure 5 are the Raman spectra of azure B and poly(azure B) prepared at the potential range of 0 and 1.10 V, respectively. The peaks at 1628 and 1496 cm^{-1} on spectrum line 1 are attributed to the stretching vibrations of C═C and/or C═N in aromatic rings. They also appear on spectrum line 2, but the peak at 1496 cm^{-1} becomes weak. The peak at 1392 cm^{-1} (strong) on spectrum line 1 is attributed to the asymmetric -CH_3 bending vibration in dimethyl groups (21). This peak also appears on spectrum line 2. This proves that -CH_3 group was not altered after polymerization. Three peaks at 954, 773 and 606 cm^{-1} are attributable to aromatic ring deformation on spectrum lines 1 and 2 (22). However, all of the three peaks become weak on spectrum line 2. The strongly sharp peak at 485 cm^{-1} is attributed to phenyl ring deformation vibration, and is characteristic of a compound with the aromatic ring(s) (20). The peak at 443 cm^{-1} on spectrum line 1 is ascribed to ring deformation. This peak on spectrum line 2 is also smaller than that on spectrum line 1. After polymerization, an obvious peak at 1429 cm^{-1} is attributed to -$N(CH_3)_2$ in poly(azure B), which is similar to an obvious peak at 1420 cm^{-1} attributed to -$N(CH_3)_2$ in poly(neutral red) (14) and an obvious peak at 1429 cm^{-1} attributed to -$N(CH_3)_2$ in poly(methylene blue) (20). The intensity of the five peaks at 1496, 954, 773, 606 and 443 cm^{-1} is much weaker. The differences between curve 1 and curve 2 mean that azure B is polymerized after electrolysis. The above results indicate that the ring of azure B molecule was not opened after polymerization.

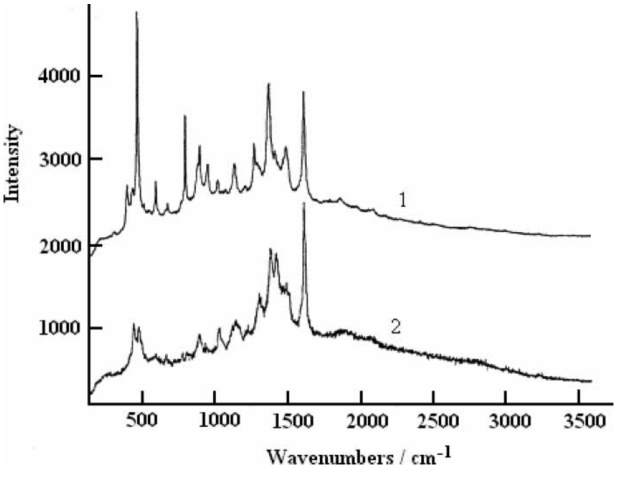

Fig. 5. Raman spectra for azure B and poly(azure B). Spectrum lines: (1) azure B, (2) poly(azure B).

3.5 *Possible Mechanism for Electropolymerization of Azure B*

Based on the above experimental results, a possible mechanism of electropolymerization of azure B was therefore proposed as follows in Figure 6. At lower applied potentials, the redox reaction between azure B (structure A) and 5-hydrogen azure B (structure B) may take place as shown in Equation (1) (5, 8), which corresponds to the pair of redox peaks at a lower potential range in Figure 1. However, at higher applied potentials the process of polymerization occurs, which is attributed to the oxidation of azure B monomer to a radical cation (structure C in Equation 2). The radical cation (C) is unstable and can lose a proton to form a free radical (structure D in Equation 3), which can further react each other to form a dimer (structure E in Equation 4), or react with another monomer to form the other radical (structure F in Equation 5). In such a consecutive way, the final poly(azure B) film can be obtained on the surface of Pt work electrode. However, the above possible mechanism still needs to be verified by other experimental techniques.

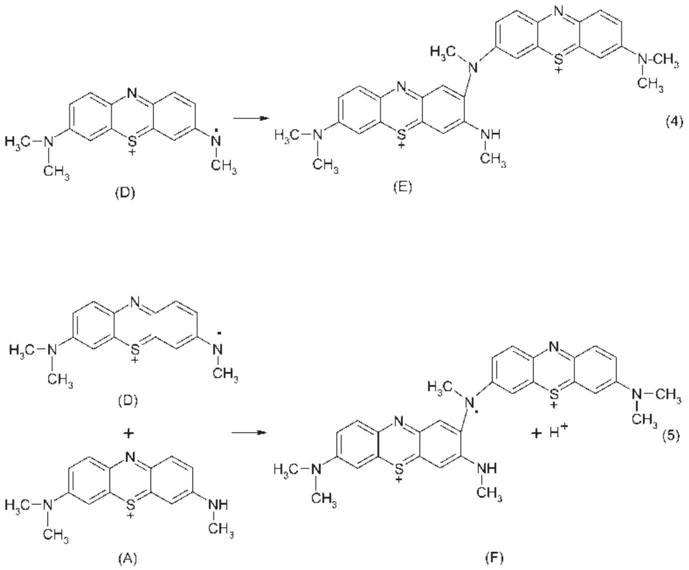

Fig. 6. Possible mechanism of electropolymerization of azure B.

4 Conclusions

A blue film, i.e., poly(azure B) has been synthesized by the electropolymerization of azure B from the solutions of the strong acid using repeated potential cycling. Poly(azure B) has good electrochemical reversibility, stability and fast charge transfer characteristics in the pH range of 1.0 to 4.0. Therefore, poly(azure B) could be a good candidate for biomaterials to immobilize enzyme. Although the polymerization mechanism is suggested here, the real synthesis mechanism and structure of poly(azure B) are rather complicated. Thus, further study for the polymerization mechanism of azure B and structure of poly(azure B) is required.

5 Acknowledgements

This work was supported by the Social Development Foundation of Zhenjiang (No.SH2006076). Thanks are given to Professor Shaolin Mu (Department of Chemistry, Yangzhou University) for the use of his laboratory facilities.

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