Electrochemical Polymerization of Brilliant Cresyl Blue and Properties of the Polymer

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The electrochemical polymerization of brilliant cresyl blue (BCB) has been carried out using cyclic voltammetry in the potential region between −0.20 V and 1.15 V (vs. Ag/AgCl with saturated KCl solution). The electrolytic solution consisted of BCB (0.1 mol/L) and Na_2HPO_4 (0.2 mol/L) with pH 2.1. BCB can not be polymerized at pH < 1. There are an anodic peak and a cathodic peak on the cyclic voltammogram of poly (BCB) at pH ≤4.3. Both peak potentials shift towards more negative with increasing pH value, and their peak currents decrease with increasing pH value. Poly(BCB) depicts a good electrochemical reversibility, fast charge transfer ability and stability in aqueous solutions with pH≤4.3. The visible spectrum, FTIR spectrum and Raman spectrum of poly(BCB) are different from those of BCB.

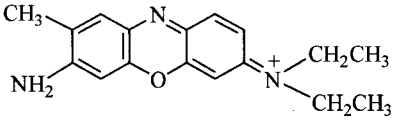
Keywords electrochemical polymerization, poly(brilliant cresyl blue), electrochemical properties, visible spectra, FTIR spectra, Raman spectra

Introduction

The discovery of the conductivity of polyacetylene has opened a new research field for the synthesis of new materials. Conducting polymers can be synthesized by the chemical polymerization and electrochemical polymerization.[1-7] The electrochemical polymerization provides a simple and fast way for their synthesis, especially, this method does not require oxidants. So the environmental pollution will be reduced. In addition, the product obtained in this way can be readily separated from the reaction mixture and has a high purity with unique properties.

Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new system. It can quickly diagnose whether a monomer can be polymerized electrochemically or not. We use cyclic voltammetry to look for new conducting polymers from over eighty monomers. Among them, it was found that several new monomers including brilliant cresyl blue (BCB) can be polymerized. The structure of BCB is as follows (Scheme 1):

Scheme 1



Recently, Karyakin *et al*. reported that azines can be polymerized.[8] Among them, the electrochemical polymerization of methylene blue,[9,10] azure B,[11,12] methylene green[13] and thionine[14] has been reported in detail. And these polymers have a good reversibility and fast charge transfer ability in a wide pH range. Thus, they can be used as biomaterials. BCB was briefly mentioned to be polymerized, but no experimental results about its polymerization and polymer properties were presented in their paper.[8] In this paper, the conditions of the electrochemical polymerization of BCB, UV-visible spectrum, FTIR spectrum, Raman spectrum and electrochemical properties of poly(BCB) were reported.

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Experimental

Chemicals and equipment

The chemicals used were all of reagent grade. Doubly distilled water was used to prepare solutions. The pH values of the solutions were determined using a PXD-12 pH meter.

The electrolysis cell for the electrochemical polymerization of BCB consisted of two platinum foils and a reference electrode. The electrolytic solution for polymerization consisted of BCB (0.1 mol/L) and Na_2HPO_4(0.2 mol/L) with different pH values. The pH value of the solution was adjusted using phosphoric acid. The area of the working electrode was 4×4 mm^2. Potentials given here were referred to the Ag/AgCl electrode with saturated KCl solution. The electrolysis was performed using cyclic voltammetry in the potential region between -0.2 V and 1.15 V. Cyclic voltammetry was carried out using an HPD-1 A potentiostat-galvanostat. A YEW 3806 X-Y recorder was used to record the cyclic voltammograms. The scan rate was 80 mV/s. The temperature was set at 30 ℃.

Measurement of spectra

The measurement of the visible spectrum of poly(BCB) film polymerized electrochemically on an indium-tin oxide (ITO) glass was carried out using a UV-2501 PC spectrophotometer. FTIR spectra of BCB and poly(BCB) were measured on pressed pellets with KBr using a Nicolet 740 FTIR instrument. Lab Ram 2 spectrometer was used for the determination of Raman spectra of BCB and poly(BCB). The latter was polymerized electrochemically on a platinum foil. All samples of poly(BCB) film were washed thoroughly using doubly distilled water before the determination of the above spectra.

Results and discussion

Electrochemical polymerization of BCB

Fig. 1 shows the cyclic voltammograms for electrolysis of the solution containing BCB (0.1 mol/L) and Na_2HPO_4(0.2 mol/L) with pH 0.7. There are three anodic peaks at 0.17 V, 0.32 V and 1.0 V and two cathodic peaks at 0.12 V and 0.24 V in Fig. 1. Their anodic peak currents decrease slowly with increasing the number of potential cycles. However, the currents of the two cathodic peaks change hardly with increasing the number of potential cycles. After fifty cycles, no polymer layer was found at the working electrode.

The *I-E* curve in the inset in Fig. 1 is the cyclic voltammogram of the above solution in the potential region between -0.2 V and 0.5 V. There are two anodic peaks at 0.17 V and 0.32 V and two cathodic peaks at 0.07 V and 0.24 V. After electrolysis, no polymer layer was found in this potential region. Comparison of Fig. 1 and the inset in Fig. 1 shows that two pairs of redox peaks at the potentials less than 0.4 V are caused by the redox of BCB itself. This is similar to the electrochemical redox of methylene blue[10] and methylene green[13] at the same potential range.

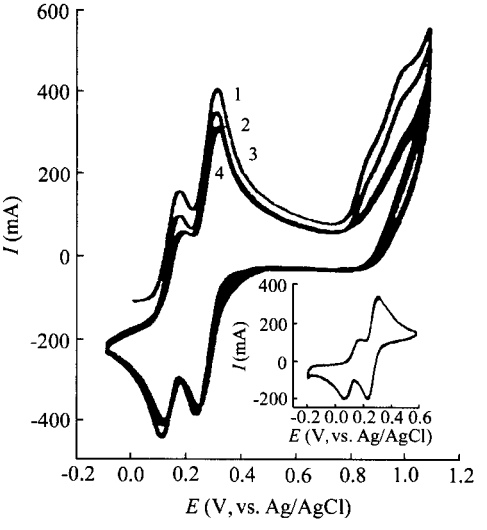


Fig. 1 Cyclic voltammograms for electrolysis of the solution containing BCB (0.1 mol/L) and Na_2HPO_4(0.2 mol/L) with pH 0.7, at 30 ℃. Curves: (1) the first cycle, (2) the second cycle, (3) the fortieth cycle, (4) the fiftieth cycle.

Fig. 2 shows the cyclic voltammograms for electrolysis of the solution containing BCB (0.1 mol/L) and Na_2HPO_4(0.2 mol/L) with pH 2.1. There are two anodic peaks at 0.18 V and 1.12 V and a cathodic peak at 0.08 V in Fig. 2. It is clear that the difference between Fig. 1 and Fig. 2 is that only a pair of the redox peaks appears in Fig. 2 in the lower potential region, and the anodic peak potential at 0.18 V shifts gradually towards

more positive and the currents of anodic and cathodic peaks decrease quickly with increasing the number of potential cycles. Both the shift of the anodic peak potential and decrease of peak currents may be caused by the formation of a film with lower conductivity on the working electrode. After fifty cycles, a blue film was found on the working electrode, which indicate the formation of poly-(BCB).

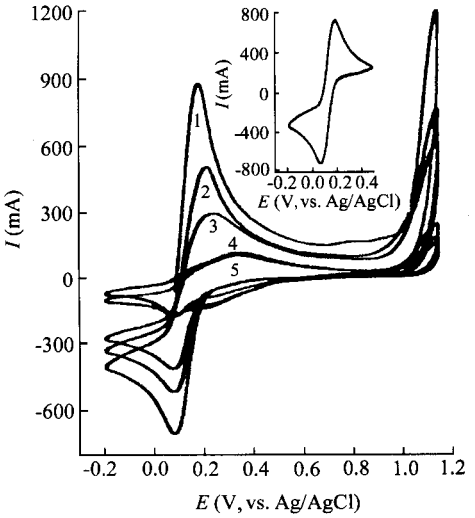
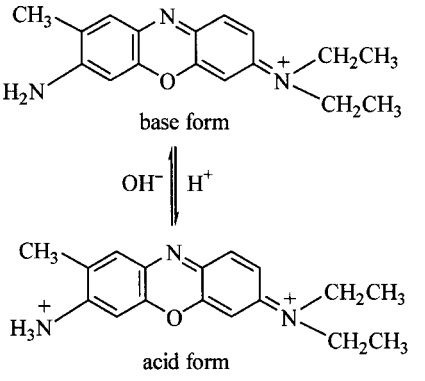


Fig. 2 Cyclic voltammograms for electrolysis of the solution containing BCB (0.1 mol/L) and Na_2HPO_4 (0.2 mol/L) with pH 2.1, at 30 ℃. Curves: (1) the first cycle, (2) the second cycle, (3) the third cycle, (4) the fortieth cycle, (5) the fiftieth cycle.

The *I-E* curve in the inset in Fig. 2 is the cyclic voltammogram of the overlapped curves of the first and fiftieth cycles in the same solution as shown in Fig. 2, but its scan potential range was set between −0.2 V and 0.5 V. There are only one anodic peak at 0.18 V and one cathodic peak at 0.08 V in the cyclic voltammogram. The anodic and cathodic peak potentials in the inset are the same as those of the first cycle in Fig. 2. This means that a pair of redox peaks at the potential less than 0.4 V in Fig. 2 is also caused by the redox of BCB itself. The difference between the inset in Fig. 2 and Fig. 2 is that in the inset the first cycle and the fiftieth cycle are overlapped completely. This indicates that the redox of BCB in the potential region between −0.2 V and 0.5 V is reversible, but is irreversible in the potential region between −0.20 V and 1.15 V, because of the formation of poly(BCB) on the electrode.

The difference between Fig. 1 and Fig. 2 is caused by the pH value of the solution. The structure of BCB may be affected by pH value (Scheme 2):

Scheme 2



At lower pH value, BCB is protonated to become an acid form. A protonated molecule is more difficult to be oxidized than an unprotonated one. This is a possible reason why BCB can not be polymerized in the solution of pH 0.7.

Fig. 3 shows the cyclic voltammograms for electrolysis of the solution containing BCB (0.1 mol/L) and Na_2HPO_4 (0.2 mol/L) with pH 7.2. A strong anodic peak appears at −0.1 V, and a corresponding cathodic peak at −0.16 V. This is in agreement with the oxidation and reduction peaks of BCB (the inset in Fig. 3). The difference between Fig. 3 and the inset in Fig. 3 is only that the peak currents and peak potentials in the inset are independent of the cycling numbers. As the potential continues to scan towards the positive direction, the oxidation current increases quickly at about 0.75 V, and then an anodic peak appears at 0.95 V. This indicates that BCB was oxidized again. After the first cycle, the anodic peak potential shifts from −0.1 V to 0 V and its peak current decreases with increasing the number of potential cycles. Finally, a blue film was found on the working electrode, which indicated the formation of poly-(BCB).

Fig. 2 and Fig. 3 show that the anodic peak potential of BCB at less than 0.4 V shifts towards more positive with increasing the number of potential cycles, however, the corresponding cathodic peak potential does not change and only the peak current decreases with increasing the cycling numbers. This is because a poly(BCB) layer with lower conductivity was formed on the platinum electrode after the first cycle, which leads to a shift of the anodic

peak potential towards more positive and decrease of anodic and cathodic peak currents with increasing cycling numbers. The question is why the cathodic peak potentials in Figs. 2 and 3 do not change with cycling numbers. A possible reason is that the reduction of BCB is affected a little by the electrode material in this case. However, the oxidation of BCB is affected significantly by the electrode material based on the results from Figs. 2 and 3. Fig. 1 shows that the oxidation and reduction peak potentials of BCB hardly change and their peak currents are very slightly affected by cycling numbers. This is because poly(BCB) was not formed during the electrolysis in the wide potential range. So the redox of BCB in this case was still carried out on platinum. The situation for the redox of BCB was changed in Figs. 2 and 3, in which poly(BCB) was formed on platinum after the first cycle. The effective area of platinum decreases with increasing cycling numbers, which leads to the increase in the polarization of the electrode. As a result, the shift of the anodic peak potential is towards more positive. Also this is why the poly(BCB) film is very difficult to grow continuously.

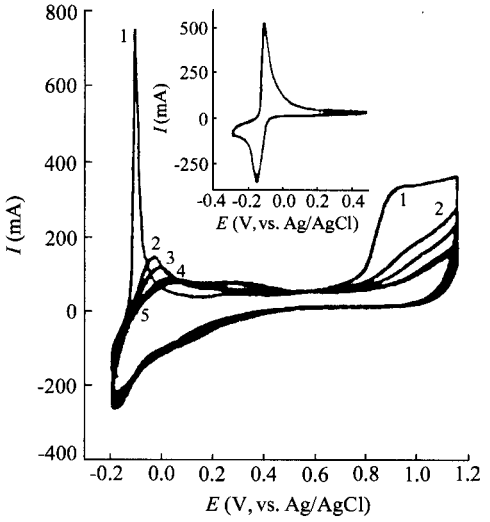


Fig. 3 Cyclic voltammograms for electrolysis of the solution containing BCB (0.1 mol/L) and Na_2HPO_4 (0.2 mol/L) with pH 7.2, at 30 ℃. Curves: (1) the first cycle, (2) the second cycle, (3) the third cycle, (4) the fortieth cycle, (5) the fiftieth cycle.

The experiment of the electrochemical polymerization of BCB was performed in the pH region between 0.7 and 7.6 in this work. However, it was found that BCB could not be polymerized at pH < 1, and the synthesis of the electrochemical property of poly(BCB) at pH region of 2 and 7.6 was a little different. Thus, poly(BCB) film used for the following experiments was obtained at pH 2.1.

Visible spectra

Curves 1 and 2 in Fig. 4 are the visible spectra of the solution of BCB dissolved in Na_2HPO_4 (0.2 mol/L) with pH 2.1, and a dried poly(BCB) film deposited on the ITO glass, respectively. There is a peak at 632 nm on curve 1. After polymerization, a broad band appears at 612 nm, which is a little shorter than that of BCB. This result is very similar to the electrochemical polymerization of methylene green.[13] In general, the wavelength of the absorption peak of a polymer could be longer than that of a monomer, since the conjugation bond distance in the polymer is much longer than that of the monomer. However, the absorption peak wavelength of BCB is a little longer than that of poly(BCB) as mentioned above. This is may be caused by the change of auxochromes in BCB after polymerization.

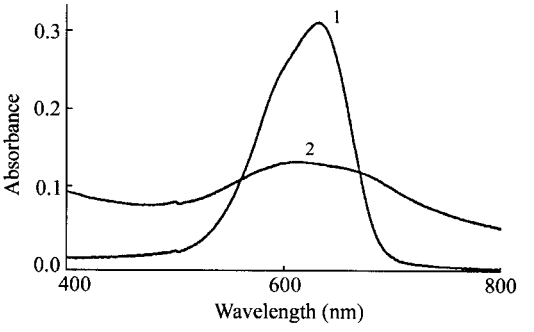


Fig. 4 Visible spectra. Spectrum: (1) BCB, (2) Poly(BCB).

FTIR *spectra*

Fig. 5 shows the FTIR spectra of BCB (spectrum 1) and poly(BCB) (spectrum 2). The FTIR spectrum 1 of BCB is very complicated. After polymerization, a strong peak at 3432 cm^{-1} attributable to stretching vibrations of N—H appears in spectrum 2, which gives us a clue that the N—H bond is still contained in the poly(BCB), and this bond is likely to be at the chain terminal of poly(BCB). The peaks at 3000 cm^{-1} and 2955 cm^{-1} are ascribed to the stretching vibrations of C—H in CH_3 and

CH_2 of BCB, respectively. However, the peak at 3000 cm^{-1} in spectrum 2 is very weak with respect to the peak at 2909 cm^{-1}, and a new peak at 2841 cm^{-1} appears in spectrum 2. The latter may be attributed to the stretching vibration of C—H in the alkyl group.

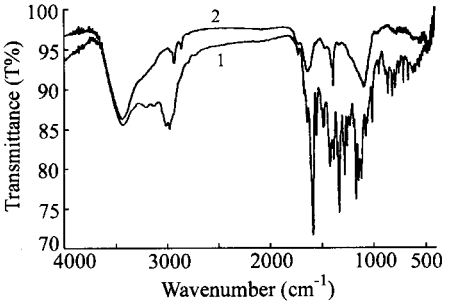


Fig. 5 FTIR spectra. Spectrum: (1) BCB, (2) Poly(BCB).

A strong peak at 1580 cm^{-1} and two weak peaks at 1636 cm^{-1} and 1443 cm^{-1} in spectrum 1 are attributed to all stretching vibrations of C = C in aromatic rings of BCB. But only a peak at 1636 cm^{-1} appears in spectrum 2, and two peaks at each side of this peak almost disappear. This is caused by polymerization. There are only two main peaks between 1400 cm^{-1} and 1000 cm^{-1} in spectrum 2, in which the peaks at 1386 cm^{-1} and at 1091 cm^{-1} are ascribed to the alkyl C—H bending vibrations and in-plane C—H bending for aromatic rings in poly(BCB), respectively. However, many peaks in this wavenumber region appear in spectrum 1. They are mainly caused by spectrum splitting because of the interaction between the different C—H bonds in CH_2 and CH_3 groups included in the monomer. Also, the prominent peaks around 840 cm^{-1} appear in spectrum 1, which are caused by out of plane C—H bending vibrations for aromatic rings. However, the intensity of these peaks in spectrum 2 are minimized obviously, and even these peaks can not be distinguished.

The FTIR spectra of BCB and poly(BCB) show that the bending vibration models of C—H in CH_2 and CH_3 are reduced after polymerization. This is main indication of the polymerization of BCB, because of the formation of chain and increment of molecular weight for the polymer. Especially, a strong absorption at 1159 cm^{-1} in spectrum 1 can be attributed to the stretching vibration of C—N in $(C_2H_5)_2=N^+$, since the stretching vibration of C—N in $(C_2H_5)_2NH$ occurred at 1140 (s) cm^{-1}.[15] However, this peak disappears in spectrum 2. This indicates that there is no C_2H_5 groups in poly(BCB), *i.e.*, C—N bond in $(C_2H_5)_2=N^+$ was broken after the polymerization of BCB.

The above results indicate that N—H bonds and CH_3 groups are still contained in poly(BCB) (spectrum 2 in Fig. 5). This means that the polymerization of BCB is not able to take place in these two positions. However, the C—N bonds disappear in spectrum 2 and the intensity of the peaks around 840 cm^{-1} in spectrum 2, attributable to the out of plane C—H bending vibrations for aromatic rings, decreases markedly. So the polymerization of BCB is suggested to be carried out via the coupling of C in the aromatic ring and N in $(C_2H_5)_2=N^+$ in BCB. It seems that the polymerization of BCB is somewhat similar to that of methylene blue,[8] in which the polymerization of methylene blue is suggested via both the coupling of C in the aromatic ring and N in $(NH_3)_2N-$, and the coupling of C and C in the aromatic rings.

Raman spectra

Spectra 1 and 2 in Fig. 6 show the Raman spectra of BCB and poly(BCB), respectively. The feature that they have in common is that a strongly sharp peak at 591 cm^{-1} appears in spectra 1 and 2. This peak is a characteristic one of BCB,[16] which was used for a sample of testing an integrated single-fiber surface-enhanced Raman scattering SERS sensor.[16] A new peak at 462 cm^{-1} appears in spectrum 2, which may be attribute to the skeletal vibrations of finite chain in poly(BCB). Therefore the new peak is a characteristic for polymerization of BCB.

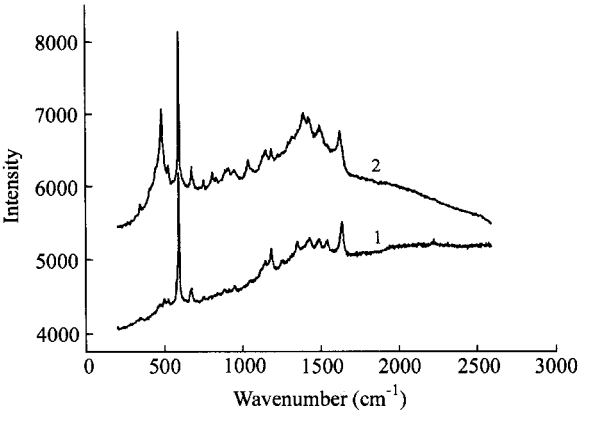


Fig. 6 Raman spectra. Spectrum: (1) BCB, (2) Poly(BCB).

Electrochemical properties of poly(BCB)

The cyclic voltammetry of poly(BCB) was carried out at 20 ℃. The scan rate was controlled at 60 mV/s. Curves 1, 2, 3 and 4 in Fig. 7 show the cyclic voltammograms of poly(BCB) in HCl (1 mol/L) solution and in NaCl (0.5 mol/L) solution with pH 1.7, 3.0 and 4.3, respectively. An anodic peak potential E_{pa} and a cathodic peak potential E_{pc} of poly(BCB) in HCl (1 mol/L) solution are 0.30 V and 0.24 V, respectively. That is, the separation of peak potentials, $E_{pa} - E_{pc}$, is 60 mV. This

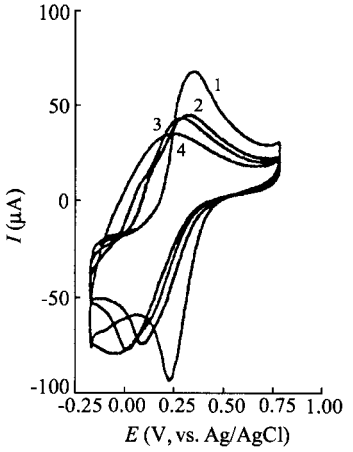


Fig. 7 Cyclic voltammograms of poly(BCB), at 20 ℃. Curves: (1) HCl (1 mol/L) solution, and NaCl (0.5 mol/L) solution, (2) pH 1.7, (3) pH 3.0, (4) pH 4.3.

indicates that the redox of poly(BCB) in this solution is one-electron reaction. Both the anodic peak potential and cathodic peak potential shift towards more negative and the separation of the peak potentials, $E_{pa} - E_{pc}$, increases with increasing pH value. 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 during the oxidation process, and vice versa for the reduction process. Also, their anodic peak currents decrease with increasing pH value. This indicates that the electrochemical activity of poly(BCB) decreases with increasing pH value. However, it still has a rather good electroactivity at pH 4.3. This property is better than that of polyaniline. The electrochemical activity of polyaniline is almost lost at this pH value.[17] Since the conductivity and the charge transfer rate of poly(BCB) decrease with increasing the pH value, the separation of the anodic and cathodic peak potentials increases with increasing the pH value. But this behavior does not affect the electrochemical reversibility of poly(BCB). It is evidence that when the poly(BCB) electrode was returned into the solution of HCl (1 mol/L) after the determination in the solution of pH 4.3, its *I-E* curve is the same as that of curve 1 in Fig. 7. So poly(BCB) has a good electrochemical reversibility at pH $\leqslant$4.3.

Fig. 8(a) and 8(b) show the effect of the scan rate on the cyclic voltammograms of poly(BCB) in HCl (0.5 mol/L) solution and NaCl (0.5 mol/L) solution with pH 3.5, respectively. The scan rate (v) was controlled between 25 mV/s and 600 mV/s. In Fig. 8(a) and 8(b),

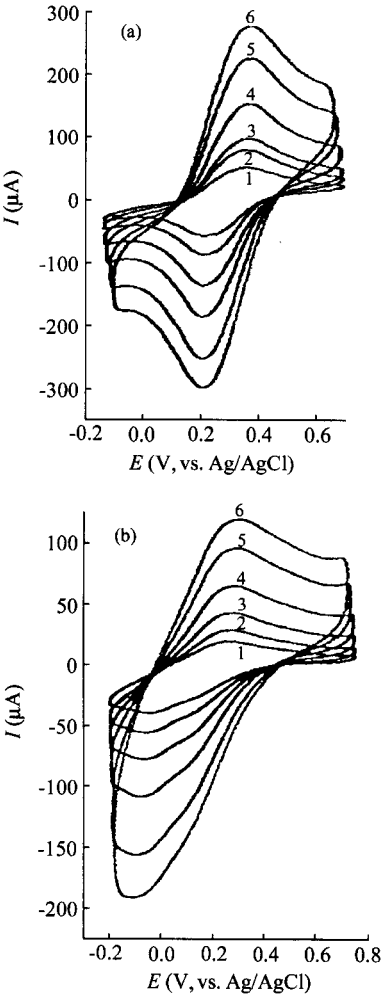


Fig. 8 Effect of scan rate on the cyclic voltammograms of poly (BCB) in (a) HCl (0.5 mol/L) solution and (b) NaCl (0.5 mol/L) solution with pH 3.5. At various scan rates. Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400, (6) 600 mV / s, at 20 ℃.

both the anodic peak potential and cathodic peak potential are independent of scan rate in this scan rate range. This means that poly(BCB) in both solutions has a good electrochemical reversibility and a fast charge transfer characteristic. Based on Fig. 8(b), plots of anodic peak current (line 1) and cathodic peak current (line 2) versus $v^{1/2}$ were constructed, which show two straight lines (Fig. 9), indicating that the electrode reaction rate of poly(BCB) was controlled by mass diffusion.

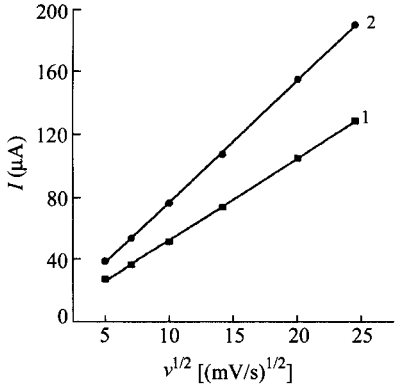


Fig. 9 Plots of peak current against $v^{1/2}$ using the data in Fig. 8(b). Curves: (1) anodic peak current, (2) cathodic peak current.

Curves 1 and 4 in Fig. 10(a) show the cyclic voltammograms of poly(BCB) in HCl (0.5 mol/L) solution at the first cycle and the fiftieth cycle, respectively. Two curves are almost overlapped completely. Curves 1 and 4 in Fig. 10(b) show the cyclic voltammograms of poly(BCB) in NaCl (0.5 mol/L) solution with pH 3.0 at the first cycle and the fiftieth cycle. After fifty cycles, only a little decrease in the cathodic peak current was observed. The above results prove that poly(BCB) has a good stability and a good electrochemical reversibility.

The above electrochemical properties of poly(BCB) were obtained from poly(BCB) polymerized on platinum. It was found that the electrochemical properties of poly(BCB) polymerized on ITO glass are very similar to those of poly(BCB) polymerized on platinum.

Conclusion

The electrochemical polymerization of BCB is strongly affected by pH values. BCB can be polymerized only at pH > 1. This is due to the strong protonation of BCB at pH < 1. Poly(BCB) has a good electrochemical reversibility, fast charge transfer ability and stability at pH ≤4.3. Based on the result from FTIR spectra, a polymerization mechanism is mentioned above, but this is only a suggestion. This is because the polymerization mechanism of BCB and the structure of poly(BCB) are rather complicated. Thus, a further study for the polymerization mechanism and the structure of poly(BCB) is required.

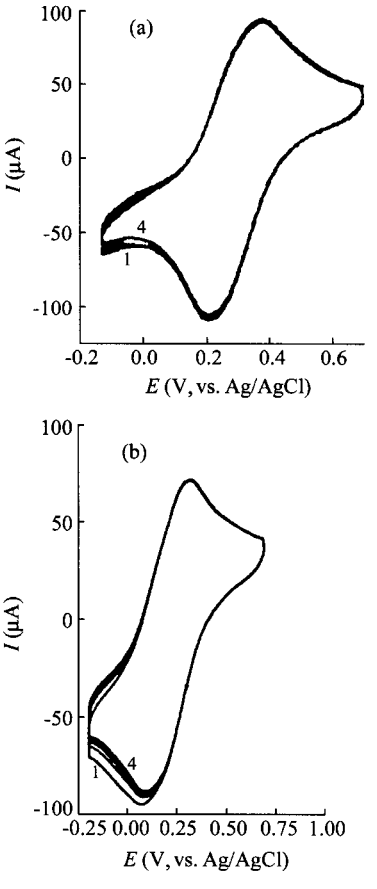


Fig. 10 Stability of poly(BCB) in (a) HCl (0.5 mol/L) solution and (b) NaCl (0.5 mol/L) solution with pH 3.0. Curves: (1) the first cycle, (4) the fiftieth cycle.

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