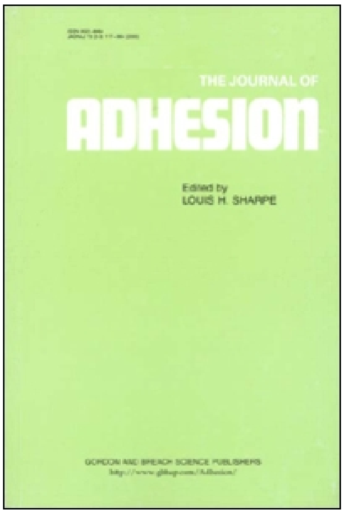

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Electrochemical synthesis and properties of polybenzoxazine

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NOTE

ELECTROCHEMICAL SYNTHESIS AND PROPERTIES OF POLYBENZOXAZINE

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A new kind of polybenzoxazine, poly(3-(p-methyl) benzyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine), has been synthesized by an electrochemical method in acetonitrile/alkali aqueous solution. The obtained film shows good heat resistance properties. The structure of the obtained film is characterized using Fourier Transform Infrared (FTIR) spectroscopy.

Keywords: Benzoxazine; Electropolymerization; Heat resistance

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INTRODUCTION

Polybenzoxazine is a novel class of polymer. The chemistry of benzoxazine dates back to the middle of the twentieth century [1–3]. Polybenzoxazines are produced from various types of substituted 3,4-dihydro-2H-1,3-benzoxazines. Ishida et al. [4, 5] and Joseph [6] have successfully prepared a series of polybenzoxazines, thoroughly investigated their structures, and proposed the possible mechanisms of polymerization.

However, as far as we know, only a few studies have focused on the electrochemical polymerization of benzoxazines. Electrochemical synthesis of polymers is a well-established technique. A number of techniques for laboratory-scale synthesis of conducting polymers, such as polypyrrole, polythiophene, and polyanline, have been employed, of which the most important are the potentiostatic and galvanostatic methods [7, 8]. In the potentiostatic method, a predetermined optimum voltage is applied during synthesis, whereas in the latter a fixed oxidation current is supplied with no control over the resulting potential of the system. Unlike conducting polymers, polybenzoxazines obtained by electrochemical methods are always insulators, are produced in extremely trace amounts and are very difficult to characterize [9]. Recently, we have successfully prepared polybenzoxazine films which could be easily removed from the electrode. This note shows the galvanostatic method for the synthesis of polybenzoxazine in acetonitrile/alkali aqueous solution. Fourier transform infrared (FTIR) spectrum indicates that the obtained polymer film has a ring-opened structure, unlike what had been reported before [9]. Thermogravimetric analysis (TGA) testing in air shows that the obtained polymer exhibits good heat resistance properties.

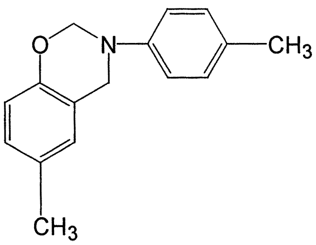
EXPERIMENTAL

Materials

The monomer, 3-(p-methyl) benzyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine, as shown in Scheme 1 (pC-a), was supplied by Professor Ishida of the Department of Polymer Science, Case Western Reserve University. All chemicals were purified before use.

Electrochemical Synthesis and Characterization

Electrochemical examination and polymerization of pC-a were performed in a one-compartment, three-electrode cell by means of an



SCHEME 1 The structure of pC-a.

EG&G model 273 potentiostat, which was under computer control. A stainless-steel sheet was used as the counter electrode and an Ag | AgCl (0.1 M KCl) electrode was used as the reference electrode in all cases. The electrochemical behavior of pC-a was examined on a platinum disc electrode (1.964×10^{-3} cm^2) as the working electrode and was analyzed using a cyclic voltammetry method. To obtain a polymer film that could be removed, a stainless-steel plate (1.5 × 4 cm) was used as the working electrode; it was polished with abrasive paper (1200 mesh) and diamond paste (1.5 μm) and then cleaned in an ultrasonic acetone bath before use. The polybenzoxazine film was deposited onto the working electrode by a galvanostatic method at a current of 1 mA/cm^2. The concentration of pC-a in conventional film preparation was 0.01 M. All solutions were de-aerated by a dry argon stream and maintained at a slight over-pressure during the experiments.

UV-visible spectra were recorded on a UV-240 spectrophotometer (Schimadzu, Japan) to investigate the change of pC-a in the acetonitrile and acetonitrile/alkali solutions. FTIR spectra were recorded on an IFS-66V spectrometer (Bruker, Germany) under vacuum. The polymer film directly used in FTIR examination was about 2–3 μm thick and was washed with acetone and dried under vacuum for 24 h at 80°C before characterization. TGA was carried out at a heating rate of 5°C/min in air on an SDT2960 thermal analyzer (TA Instruments, New Castle, Delaware, USA).

RESULTS AND DISCUSSION

Electrochemical Behavior of pC-a

Figure 1 shows the evolution of cyclic voltammetry (CV) of pC-a in acetonitrile/Bu_4NBF_4 (0.1 M) solutions. There are several anodic peaks which could not be clearly distinguished from each other beyond 1.25 V versus Ag/AgCl (0.1 M KCl); however, no cathodic peak was observed in the first cycle, which infers that the oxidation of pC-a may

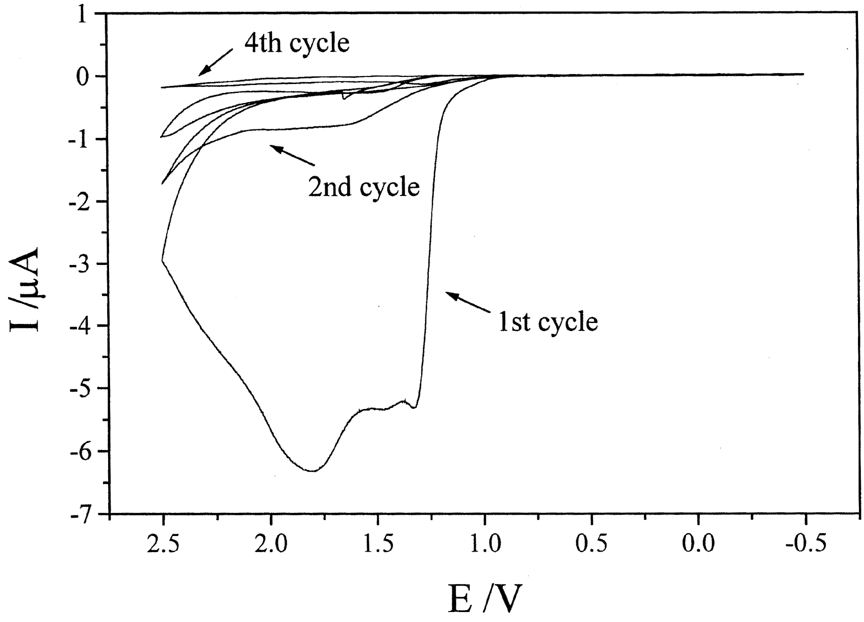


FIGURE 1 The first four CVs of pC-a in dry acetonitrile solution containing 0.1 M Bu_4NBF_4 at a potential scan rate of 20 mV/s.

involve multiple but irreversible paths. This is in accordance with the results of Audebert *et al.* [9]. The current decreases sharply in subsequent cycles, which is ascribed to the passivation of the surface of the electrode and indicates that further oxidation of pC-a has been prevented. No polymer is formed on the working electrode.

When hydroxide ions are added to the acetonitrile solutions, the colorless solution turns light yellow, which implies that there is some kind of interaction between the OH^- anion and the monomer. Figure 2 shows the UV-visible spectra of the monomer in nonalkaline (Figure 2a) and alkaline (Figure 2b) solutions. The characteristic UV-absorption peak of pC-a at 201 nm in the nonalkaline solution shifts to 208 nm in the alkaline solution. Another difference is the change of the relative intensity of the absorption peaks. When OH^- anions are added to the solution, the intensity of the absorption peak around 201 nm decreases and that of the absorption peak around 230 nm increases so greatly that the former nearly becomes a shoulder peak. It is speculated that the reason for the change is the formation of benzoxazine anions [9]:

$$\text{pC-a} + OH^- \rightarrow (\text{pC-a})^- + H_2O.$$

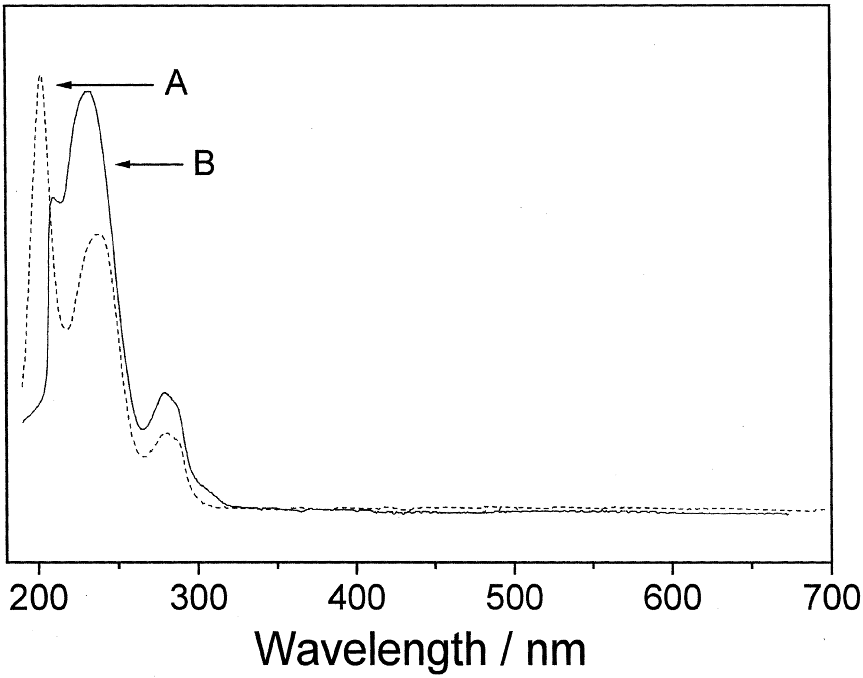


FIGURE 2 UV-visible spectra of pC-a in acetonitrile solution (a) and acetonitrile/alkaline aqueous solution (b).

We intended to lower the oxidation potential of pC-a by adding OH^- anions; however, we found that the electrochemical behavior of pC-a in acetonitrile/alkali aqueous solution, as shown in Figure 3, is different from that of benzoxazine in methanol/alkali aqueous solution, as reported by Audebert *et al.* [9]. In the first scan, the first anodic peak of pC-a in acetonitrile/alkali aqueous solution appears around 1.5 V, which is very similar to that of pC-a in pure acetonitrile solution. However, it seems to be a single-electron-transferring process. The onset potential of the second oxidation process is around 2.0 V. In subsequent cycles, the anodic peak at 1.5 V moves to about 1.25 V and becomes smaller but sharper. However, the onset potential of the second anodic process decreases and the peak current increases with increasing numbers of scans, which suggests a self-catalysis effect of the oxidation process. Polymeric product can be observed at the surface of the electrode. It is speculated that the electrochemically active species generated around 1.5 V could not result in polymer formation (because no polymer can be obtained at 1.5 V using the potentiostatic method).

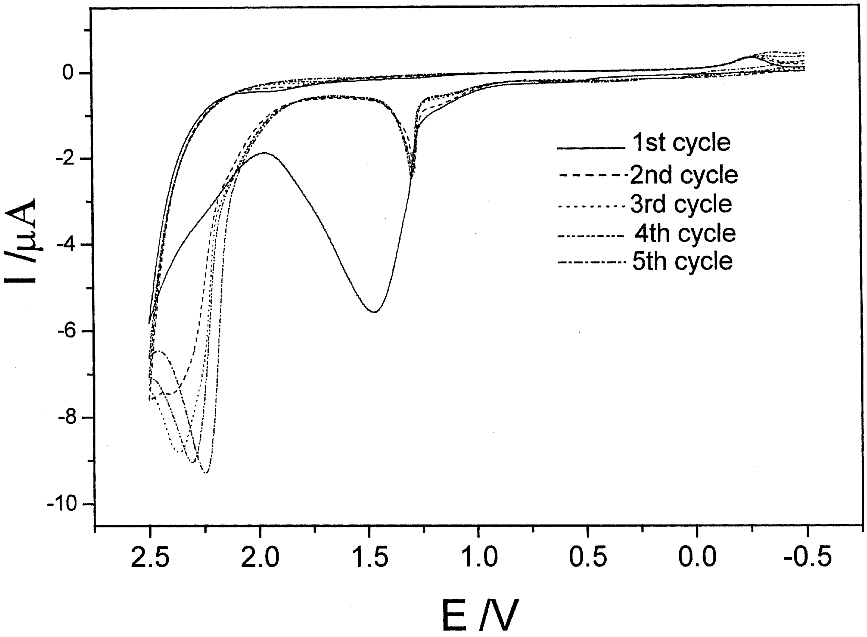


FIGURE 3 The first five CVs of pC-a in acetonitrile/alkaline aqueous solution. $V(\mathrm{MCN}) : V(\mathrm{H_2O}) = 3 : 1$, $c(\mathrm{NaOH}) = 0.1\,\mathrm{M}$, other conditions are the same as in Figure 1.

But these active species undergo further oxidation around 2.0 V and result in polymer formation. The formed polymer phase catalyzes the second oxidation process and then lowers the polymerization potential.

A dark-brown polymer film could be obtained by using the galvanostatic method. Figure 4 shows the potential-time curve during the polymerization process. There is an over-potential at the beginning, and then the polymerization potential becomes lower and is inclined to reach a steady state, which infers that the polymerization is carried out smoothly. By optimizing the polymerization conditions, the polymer film could grow up to 5 μm thick and be pulled off the electrode. (Optimized condition: current density: $1\,\mathrm{mA/cm^2}$; volume ratio of acetonitrile/water solution: 3:1; the molar ratio of NaOH/pC-a: 1:1; the temperature: 0°C.)

Structural Characterization

To our knowledge, the structure of the electrochemically synthesized polybenzoxazine has not been clearly characterized. Audebert *et al.* [9]

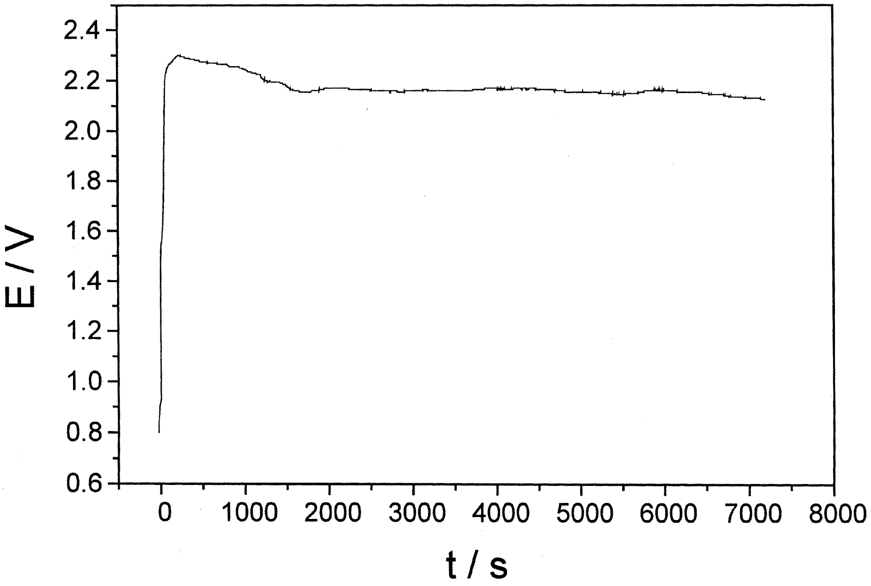


FIGURE 4 The potential-time curve of the polymerization of pC-a.

suggested a possible oxazine-ring-remaining structure for electrosynthesized polybenzoxazine. However, they did not provide convincing evidence. On the other hand, Wang and Ishida [5] proposed the possible structure of polybenzoxazine produced by a chemical method.

The FTIR spectrum of pC-a is compared with that of electrochemically synthesized Poly(pC-a) in Figure 5. The most impressive characteristic is the absorption band located around 3400 cm^{-1}. In the spectrum of Poly(pC-a), as shown in Figure 5a, the intense band located at 3360 cm^{-1} is ascribed to an OH stretching vibration. This indicates the existence of OH groups in Poly(pC-a). Furthermore, another noticeable feature is that an absorption band around 946 cm^{-1} in the monomer spectrum is a characteristic of the oxazine ring [10]. However, this band disappears in the polymer spectrum. The evolution of these two bands demonstrates the successful opening of the oxazine rings upon polymerization.

The evolution of a pair of bands around 1225 cm^{-1} and 1034 cm^{-1} in the spectra of the monomer and the polymer provides further evidence of the favored structure in electrochemical polymerization. In the spectrum of the monomer, the band around 1225 cm^{-1} is attributed to an aromatic carbon-oxygen stretching vibration, and the band near 1034 cm^{-1} is the highest aliphatic carbon-oxygen stretching mode

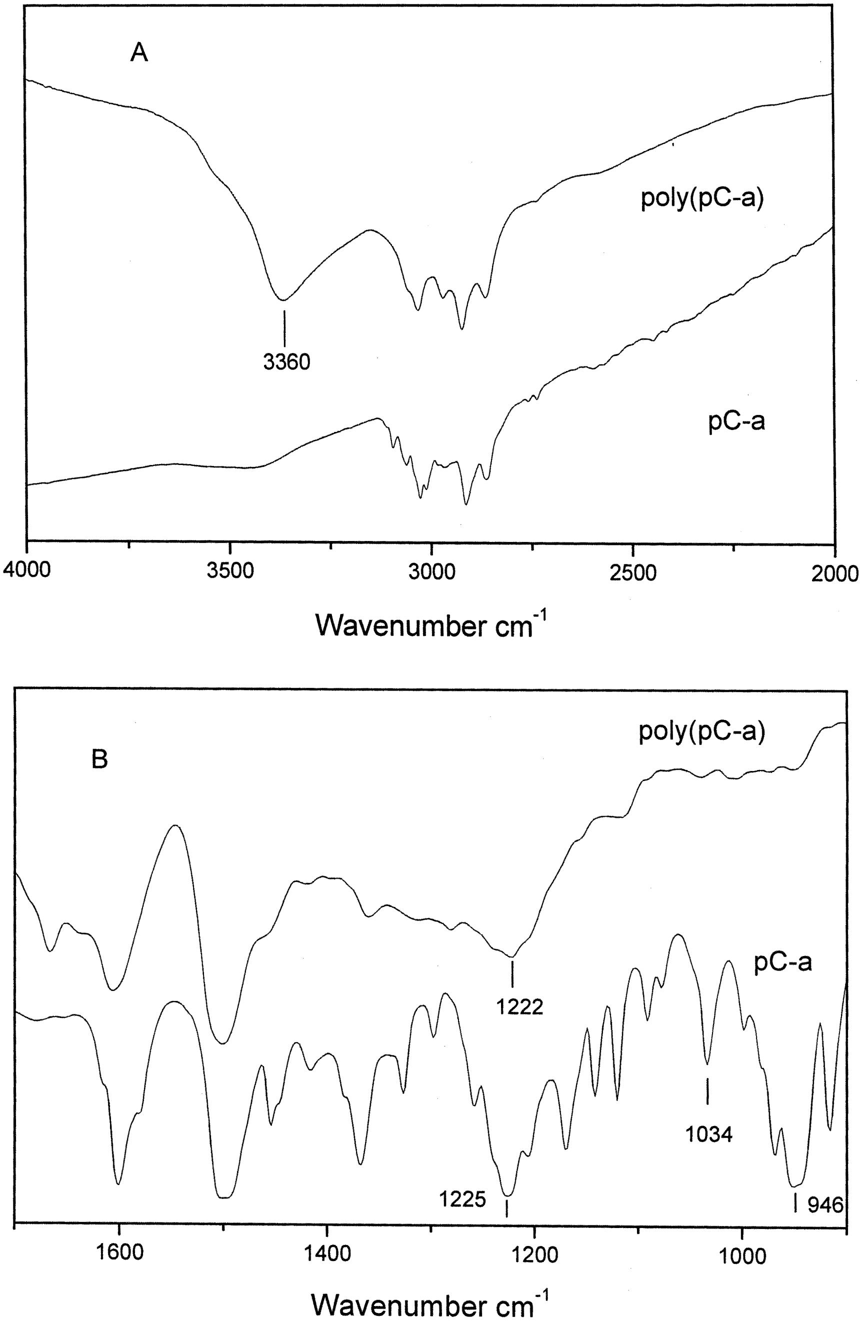


FIGURE 5 (a) 4000–2000 cm^{-1}and (b) 1700–900 cm^{-1} FTIR region of Poly(pC-a) and pC-a.

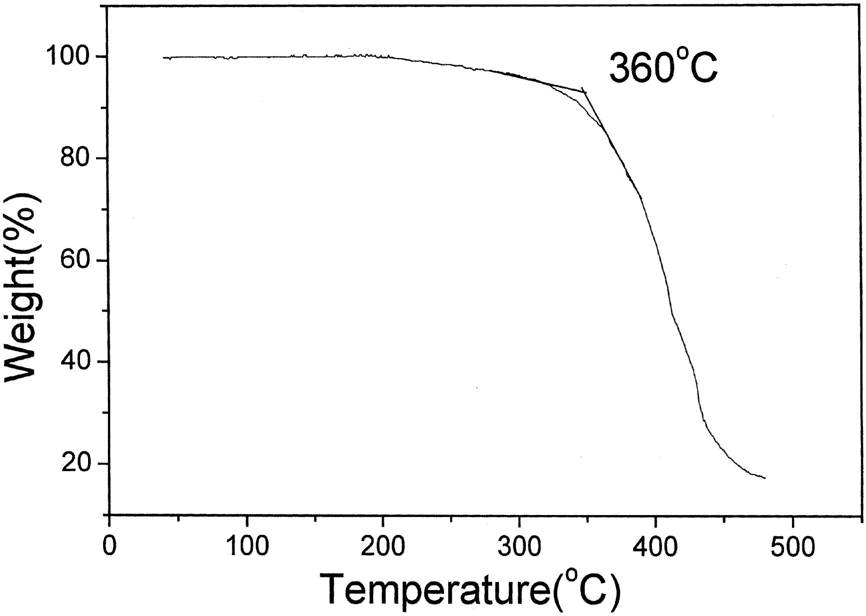
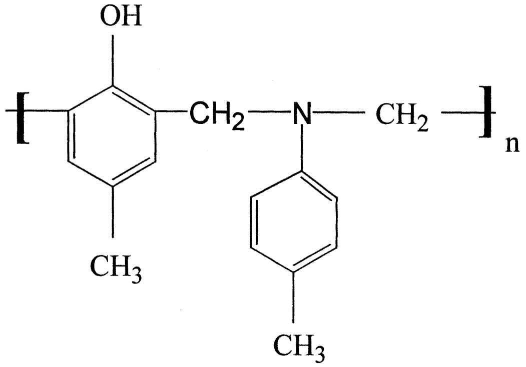


FIGURE 6 TGA curve of Poly(pC-a) at a heating rate of 5°C/min in air flow.

[11, 12]. However, the absorption around 1034 cm^{-1} disappears in the spectrum of the polymer, while the absorption around 1222 cm^{-1} almost remains the same. This infers the disappearance of aliphatic carbon-oxygen structure in the polymer. This proof, together with the characteristic band in the OH stretching region, indicates that the electrochemically-synthesized Poly(pC-a) has the structure of Type A.



TYPE-A

Thermal Resistance of Poly(pC-a)

Thermal characterization of these polymers was accomplished by TGA. The result of the TGA experiment on the polymer is shown in Figure 6. It can be seen that the polymer remains stable up to 360°C in air, which indicates that Poly(pC-a) has good heat resistance.

CONCLUSIONS

New polybenzoxazine has been synthesized by electrochemical polymerization in an acetonitrile/alkali aqueous solvent system. A reasonable structure of Poly(pC-a) has been proposed which is in agreement with all the experimental results.

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