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COPOLYMERS OF *N*-ACRYLOYL-*N*′-METHYLPIPERAZINE AND METHYL METHACRYLATE: SYNTHESIS AND ITS APPLICATION FOR Hg(II) DETECTION BY ANODIC STRIPPING VOLTAMMETRY

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Abstract—Copolymers of *N*-acryloyl-*N*′-methylpiperazine and methyl methylacrylate were synthesized and characterized. The monomer ratio in the copolymer was analyzed by FTIR spectroscopy. The copolymer was found to form a complex with Hg(II) ions. A chemically modified electrode (CME) fabricated by attaching a copolymer film to a glassy carbon electrode for the detection of Hg(II) ions is described. The polymer swelled in aqueous solution, allowing easy access of Hg(II) ion for binding. Anodic stripping voltammetry was employed for the detection of Hg(II) ions. The effects of pH of the measurement and deposition solutions, deposition time and the Hg(II) concentration were studied. The limit of detection was estimated to be 0.23 μg/ml. © 1997 Elsevier Science Ltd

INTRODUCTION

Polymers containing amino groups have been widely investigated in view of their various potential applications either as components of biomedical materials [1–3] or as constituents of drug delivery systems [4, 5]. Amino polymers containing piperazine moieties have also been extensively studied, mostly by the research groups of Barbucci, Ferruti and Ranucci [2–4, 6–8]. Piperazines are interesting diamine molecules that have been recognized as unique chelating agents, and many interesting piperazine metal ion complexes have been reported [9–13]. Indeed, poly(amido-amines) containing the unit 1,4-bisacryloylpiperazine have been shown to form complexes with Cu^{2+} and Ni^{2+} [14]. These polymers have found applications as flocculating and dispersing agents for minerals and as selective ion-exchange resins [2]. However, there has been no report of these types of polymers being applied in the fabrication of chemically modified electrodes (CMEs) for the detection of heavy metal ions. Polymer membrane-based CMEs [15–27] have been widely investigated because of their selectivity, rapid response times and ease of fabrication, especially in the application of microelectrodes [26, 27]. The membrane/film is typically made of plasticized poly(vinyl chloride) (PVC) or unplasticized silicone rubber. Other polymeric matrices used include conducting polymers, such as poly(pyrrole) and poly(aniline) [18–22]. Generally, chemical species are doped into the membrane to achieve the desired selectivity. However, most of these polymeric membranes suffered from the slow exudation of the plasticizers or/and the doped species, resulting in membrane deterioration or/and loss of sensitivity. Thus it is desirable to have the required chemical species, functional groups or ligands responsible for the selectivity incorporated directly into the polymer backbone.

In this paper, the synthesis of copolymers of poly(*N*-acryloyl-*N*′-methylpiperazine-co-methyl methacrylate) and its application in the fabrication of a chemically modified electrode (CME) for the detection of mercury (II) by anodic stripping voltammetry is described.

EXPERIMENTAL

Materials

Acryloyl chloride from Fluka was distilled under dry nitrogen and stored in the refrigerator. *N*-Methyl piperazine from Fluka was stored over molecular sieves and used as received. Methyl methacrylate from TCI was distilled at reduced pressure under nitrogen and stored in the refrigerator. Azobisisobutyronitrile (AIBN) from TCI was recrystallized in methanol. Hydroquinone dimethylether obtained from Fluka was used as received without further purification. 1,4-Dioxane (Merck) was distilled under nitrogen over metallic sodium and used immediately. Tetrahydrofuran from Baker was distilled over solid potassium permanganate and stored over molecular sieves. Triethylamine from Fluka was stored over molecular sieves and used as received. Diethyl ether from Merck was used as received without further purification. Na_2HPO_4, NaH_2PO_4 and Hg(II) (1000 μg/mL, atomic spectra standard) were obtained from Baker, and citric acid, tri-sodium citrate, HNO_3 (69%) and KNO_3 were obtained from BDH. Buffer solutions of NaH_2PO_4–Na_2HPO_4 and citric acid–sodium citrate were prepared by adjusting 0.1 M NaH_2PO_4 solution

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with Na_2HPO_4 and 0.1 M citric acid with 0.1 M sodium citrate to the required pH, respectively. Dialysis membrane (MW cut-off: 12,000) was obtained from Bethesda Research Laboratories (BRL). Glassy carbon electrode was purchased from BioAnalytical Systems Inc (BAS). Ultrafiltered de-ionized water from Barnstead ultrapure system (Model D 4755, U.S.A.) was used throughout the experiment.

Synthesis

N-Acryloyl-N′-methyl piperazine (AcrNMP). *N*-methyl piperazine (0.2496 mol, 27.7 ml) and triethylamine (0.35 mol, 48 ml) were dissolved in 400 ml of dry THF in a 1 L three-necked round-bottomed flask fitted with a nitrogen inlet and a guard tube. The flask was cooled in an ice-bath and maintained under flowing nitrogen. THF solution (75 ml) containing acryloyl chloride (0.2600 mol, 21.1 mL) was added dropwise over a period of 75 min with constant stirring. The reaction mixture was then allowed to equilibrate to room temperature and continuously stirred overnight. Triethylamine hydrochloride was removed by filtration and washed repeatedly with warm THF solution. The filtrate was concentrated using a rotary evaporator. The brown viscous liquid was distilled under reduced pressure and the 82–84°C fraction was collected, with a yield of 65%. Hydroquinonedimethyl ether solution, 0.5%, was added prior to distillation to inhibit any spurious polymerization of the monomer. ^1H NMR: δ2.30 (*s*, 3H, NCH_3), 2.37–2.49 (*m*, 2H + 2H, (CH_2N—), 3.64 (*br*, 2H + 2H, $OCN(CH_2)_2$), 5.60–5.74 (*m*, 1H, CH=C—CON<, *trans*), 6.11–6.33 (*m*, 1H, CH=C—CON<, *cis*), 6.49–6.81 (*m*, 1H, =CHCON<).

Polymerization

Poly(N-acryloyl-N′-methyl piperazine (PAcrNMP). PAcrNMP was prepared by solution polymerization using AIBN as initiator. *N*-Acryloyl-*N′*-methyl piperazine (8.74 mmol, 1.3461 g) and AIBN (0.5 wt%, 0.021 g) were dissolved in 40 mL freshly distilled dioxane in a 100 mL round bottom flask fitted with a vacuum tap. The contents were degassed by three freeze–thaw cycles. The flask was heated in an oil bath at 70°C for 24 hr with constant stirring. The viscous contents of the flask was poured into a large volume of anhydrous diethyl ether (800 mL) to precipitate the polymer. The polymer was re-precipitated in diethyl ether three times, to give a pale yellow hydroscopic powder (yield 90%). The intrinsic viscosity in water at 30°C is $[\eta] = 0.184\ \mathrm{dL/g^{-1}}$.

Copolymers of N-acryloyl-N′-methyl piperazine and methylmethacrylate (PAcrNMP-co-MMA). Copolymers of *N*-acryloyl-*N′*-methyl piperazine and methyl methacrylate were synthesized in dioxane using different monomer feed ratios and AIBN as initiator. Typically, *N*-acryloyl-*N′*-methyl piperazine (0.0161 mol) and methyl methacrylate (0.0964 mol), and AIBN (0.5 wt% based on the total weight of the monomers) were dissolved in 40 ml freshly distilled dioxane. The flask was degassed by three freeze–thaw cycles. Polymerization was carried out at 70°C, for a period of 2 days with constant stirring. The polymer was isolated by precipitating the contents of the flask in anhydrous diethyl ether (800 mL) and purified by reprecipitation from diethyl ether three times. The final product was a pale yellow powder (yield 85%). Copolymers of other AcrNMP/MMA feed ratios were similarly synthesized.

Characterization

Viscosity measurement. Intrinsic viscosities were determined in water for the homopolymer PAcrNMP and in chloroform for PAcrNMP-co-MMA copolymer at 30°C using a Cannon–Ubbehlode dilution-type viscometer.

Spectroscopic measurements. IR spectra were recorded by a Perkin–Elmer 1725-X Fourier transform infrared (FTIR) spectrometer. The NMR spectra were recorded in $CDCl_3$, on a Bruker 500 MHz and a Jeol JNM-EX90A (90 MHz) Fourier transform spectrometer.

Differential scanning calorimetric measurements. DSC measurements were recorded using a Perkin–Elmer differential scanning calorimeter DSC 7. The glass transition temperature (T_g) was determined with a scanning rate of 20°C/min.

Electrochemical measurements. All the electrochemical measurements were carried out using a computerized potentiostat/galvanostat (Model 273A, EG&G), Princeton Applied Research with Model 270/250 Research Electrochemistry Software 4.0). The three electrode assembly consisted of a 50 mL glass cell, a Ag/AgCl (saturated with KCl–AgCl), a platinum wire counter electrode, and a glassy carbon electrode.

Construction of chemically modified electrode (CME). The polymer film on the glassy carbon electrode was prepared by dipping the electrode into a 15% copolymer solution in chloroform, followed by evaporating the solvent to dryness at room temperature. The film was further covered with a dialysis membrane (MW cut-off: 12,000) which was tightly secured by a soft plastic tube as shown in Fig. 1. The electrode was left to immerse in water for at least 12 h for conditioning before use. This was to ensure that swelling of the polymer film had reached equilibrium condition.

Voltammetric measurements. Prior to voltammetric measurements, the electrolytic medium containing 50 mL of buffer with 0.1 M KNO_3 was deaerated for at least 5 min using nitrogen gas and a blanket of nitrogen was maintained during the course of the experiment. The modified electrode was conditioned by first using cyclic linear voltammetry in the range of 0.5 to −0.8 V (*V* vs Ag/AgCl) with a scan rate of 50 mV/sec for at least five times. This was followed by scanning with square wave voltammetry from 0.5 to −0.8 V, and back to 0.5 V with a frequency of 50 Hz. Chemical deposition was done by immersing the electrode in standard Hg(II) solutions for a fixed period of time with stirring at a constant rate of 500 rpm. For the voltammetric measurement, electrolytic reduction was first carried out at −0.5 V for 60 s. Square wave was then applied for the anodic stripping process sweeping from −0.5 to 0.5 V. The electrode was regenerated by immersing in 0.1 M HNO_3 solution, which served as purging solution, for 1 min at a potential of 0.5 V. This was to re-oxidise any remaining mercury. Then with the potential off, the electrode was left in the purging solution with constant stirring for a further period of 10–30 min until the mercury was fully removed.

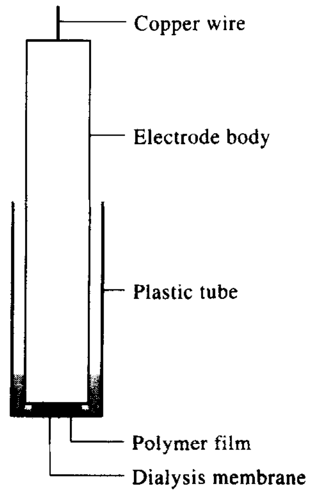
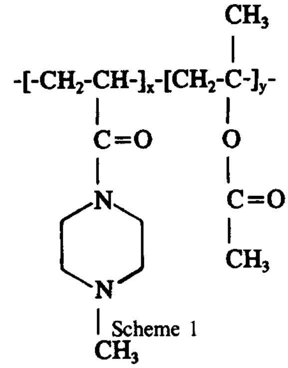


Fig. 1. Schematic drawing of the copolymer modified electrode.



Scheme 1

RESULTS AND DISCUSSION

Polymer characterization

The IR spectrum of a PAcrNMP-co-MMA (Scheme 1) is shown in Fig. 2.

The carbonyl absorptions from the MMA and AcrNMP units were fairly well separated with peak maxima at 1728 and 1638 cm^{-1}, respectively. The molar extinction coefficients for these absorptions were determined from the standard chloroform solutions of PMMA and PAcrNMP, respectively, using a liquid cell. The values were $\varepsilon_{1728} = 300 \pm 10\ dm^3\ mol^{-1}\ cm^{-1}$ for MMA and $\varepsilon_{1638} = 330 \pm 10\ dm^3\ mol^{-1}\ cm^{-1}$ for AcrNMP. Using these ε values, the ratios of AcrNMP:MMA in the copolymer were determined from the relative intensities of the carbonyl absorptions. The slight overlapping of the two absorptions were resolved by deconvolution manipulation using the IRDM software from Perkin–Elmer. Attempts to analyse the monomer ratio from the ^1H NMR spectrum were not successful because of extensive overlappings of the resonance signals of the two monomer units (Fig. 3). All the copolymers prepared with various AcrNMP:MMA ratios were soluble in chloroform. However, they were not soluble, but swelled in water. In this study, the copolymer used in the fabrication of CME for the detection of mercury(II) ions was prepared from the 1:1 monomer feed ratio. The copolymer formed was found to have the AcrNMP:MMA ratio of 1:1.9 by IR analysis. The intrinsic viscosity was $[\eta] = 0.47\ dL/g$ at 30°C in chloroform and $T_g = 106.1°C$ for the polymer was obtained.

Electrochemical response. The electrochemical response of Hg(II) of the CME prepared was investigated in citric acid–sodium citrate buffer solution (pH 3.1) by means of cyclic voltammetry and square wave voltammetry. Figure 4(A) shows the cyclic voltammograms for eight consecutive sweeps after the electrode had been immersed in 100 $\mu g/ml$ Hg(II) solution for 1 min. The cathodic peak at 0.114 V was relatively broad and the response was weak, indicating that the electron transfer rate was slow for the reduction process. In contrast, a sharper and more sensitive anodic peak at 0.250 V was observed, indicating that mercury was easily oxidized to Hg(II). The peak potentials remained relatively constant after eight consecutive sweeps. Only a negligible change in the peak current was observed. This implied that the concentration of mercury in the polymer film remained relatively constant from

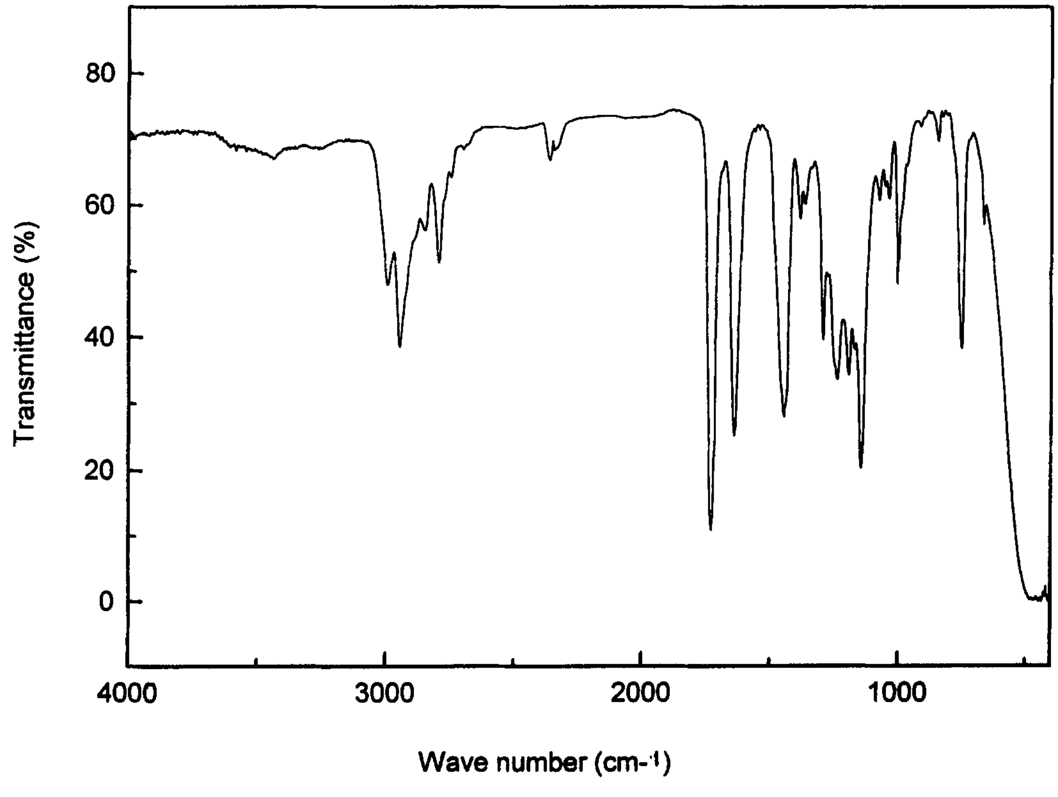


Fig. 2. FTIR spectrum of PAcrNMP-co-MMA (MMA:AcrNMP = 1:1.9) film on NaCl window.

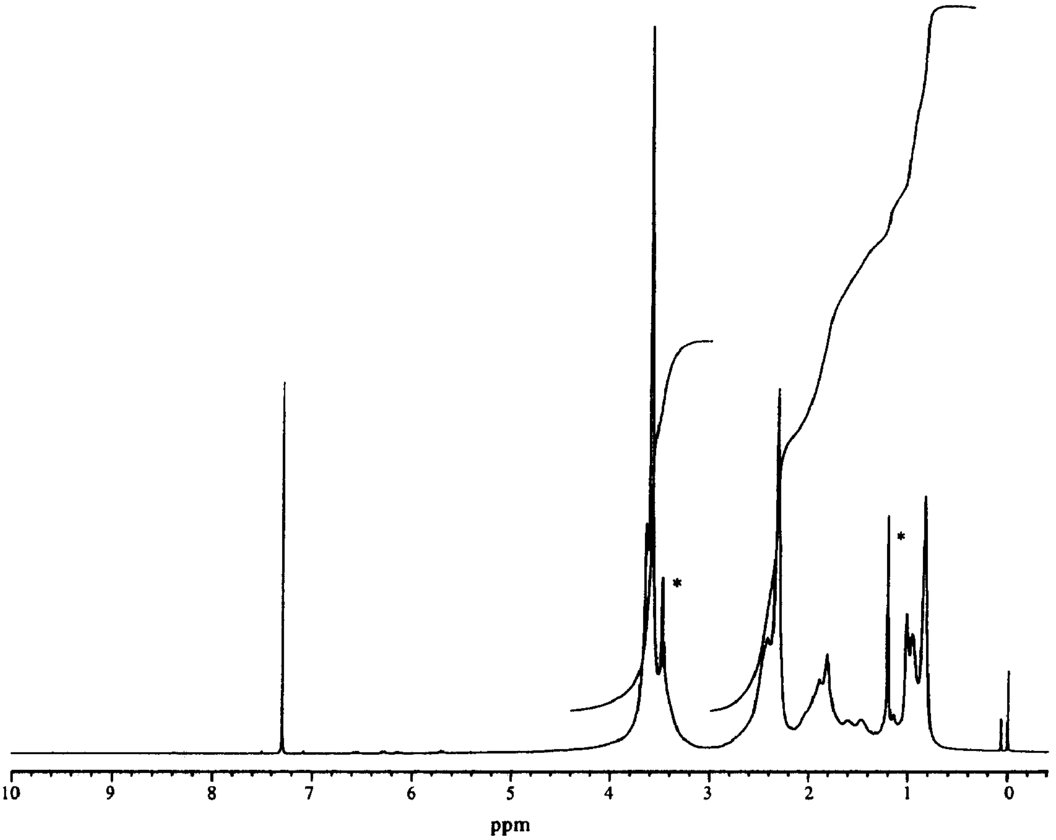


Fig. 3. ^{1}H NMR (500 MHz) spectrum of PAcrNMP-co-MMA (MMA:AcrNMP = 1:1.9) in CHCl$_3$ (*: residue diethyl ether solvent).

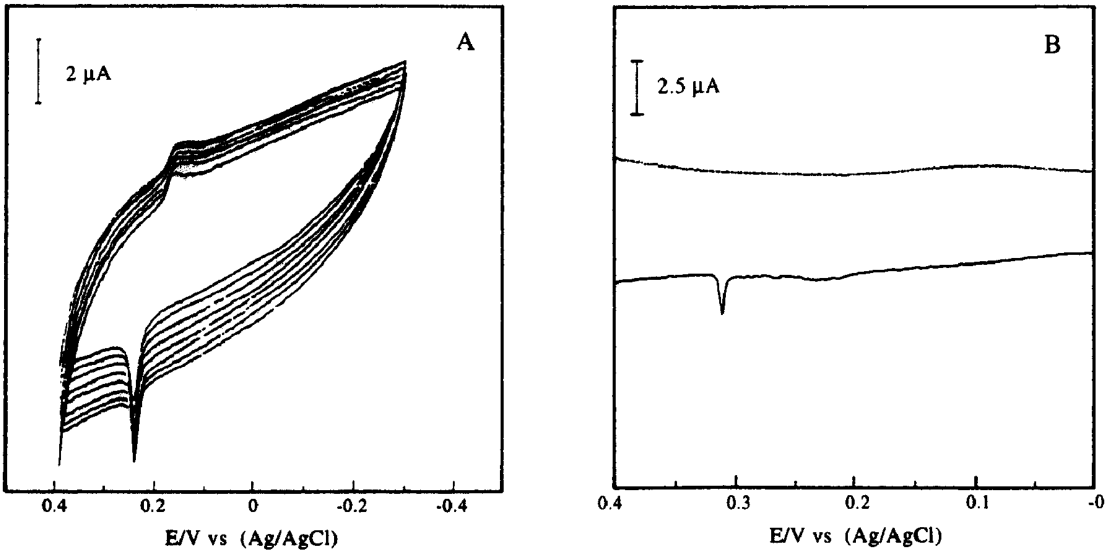


Fig. 4. (A) Cyclic voltammograms (8 scans), after 1 min chemical deposition in a 100 µg/ml Hg(II) solution and with scan rate 50 mV/s at pH 3.1. (B) Square-wave voltammograms, after 1 min chemical deposition in a 5 µg/ml Hg(II) solution with frequency 50 Hz at pH 3.1. Dotted line: cathodic scan; solid line: anodic scan.

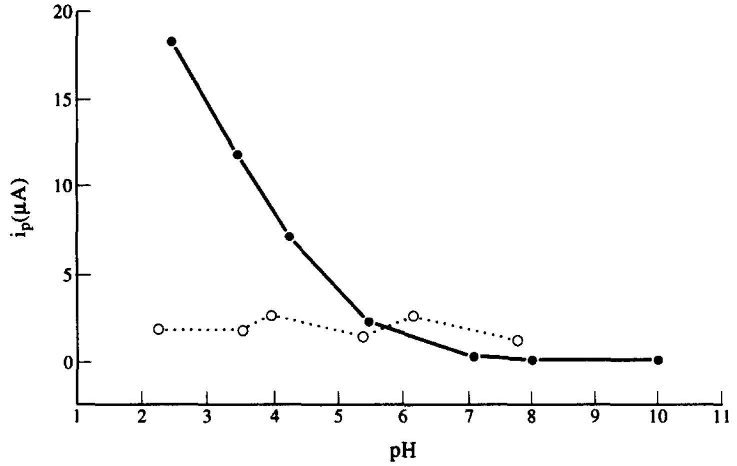


Fig. 5. Solid line: effect of pH of the measurement solutions, after 5 min deposition from 5.0 μg/ml Hg(II) solution. Dotted line: effect of pH of chemical deposition solutions containing 1 μg/ml Hg(II) ions with a deposition time of 5 min and pH 3.1 for the measurement solution.

repeated voltammetric measurements. The stability of the polymer film was thus established.

In square wave voltammetry, scaning with 50 Hz frequency from − 3 to 0.4 V produced a well-defined anodic peak with a potential at 0.303 V (solid line) after 1 min of deposition in a solution containing 5 μg/ml of mercury(II). No discernible peak was found for the cathodic process (dotted line) (Fig. 4B). Hence the stripping anodic voltammetric technique was used in all the measurements.

Effects of pH and deposition time. The pH of the measurement solution had a profound effect on the anodic stripping voltammetric response. At pH of 7.0 and above, only a small peak current was observed, but the peak current increased significantly from 1 to 17 μA as the pH decreased from 7.0 to 2.5 (Fig. 5, solid line). This effect could be attributed, at least partly, to the formation of mercury(II) hydroxide at higher pH. In contrast, the pH of the deposition solution had little effect. The peak current remained essentially constant for the chemical deposition solutions with pH ranging from 2.2 to 8.0 (Fig. 5, dotted line). Although the pH of the chemical deposition solution had negligible effect, higher pH should be avoided in order to minimize the formation of mercury(II)-hydroxide. Hence, all the experiments were carried out under the same standard conditions with measurement solutions of pH 3.1 and deposition solutions of pH 4.2.

The anodic voltammetric response also varied with the chemical deposition time under constant concentration of deposition solution. With 3.0 μg/ml Hg(II) deposition solution, a linear increase of the peak current with increasing deposition time was observed in the initial 8 min. The subsequent levelling off of the peak current signified approaching of saturation as the deposition time increased further (Fig. 6). The deposition rate was fast as indicated by the short time it took to reach saturation. With a more dilute mercury(II) solution of 1.0 μg/ml, the linear portion of the peak current extended to a longer period of time of 30 min.

Detection limit and calibration. The reproducibility of the electrode was found to be satisfactory. Results from ten measurements with 5 min of chemical deposition in 1.0 μg/ml Hg(II) solution gave an

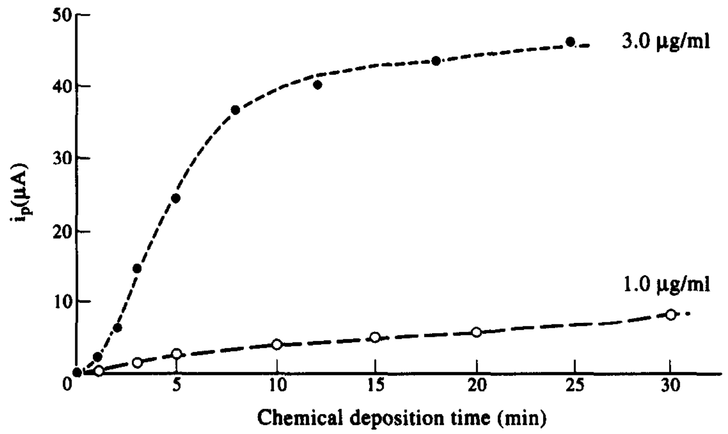


Fig. 6. Change in peak current as a function of chemcal deposition time in 1.0 μg/ml (opened circle) and 3.0 μg/ml (filled circle) Hg(II) solutions by square wave anodic stripping voltammetry with frequency 50 Hz.

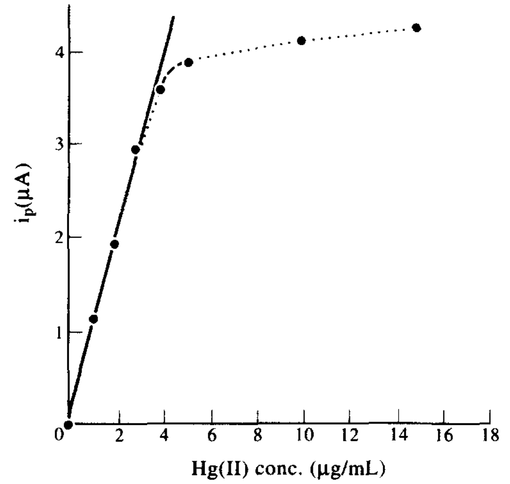


Fig. 7. The response of the copolymer modified electrode as a function of Hg(II) ions concentration measured at pH 3.1 after 5 min deposition, obtained by square-wave anodic stripping voltammetry with a frequency of 50 Hz.

average peak current of 1.67 μA and a standard deviation of 0.13 μA. This in turn yielded a value of 0.23 μg/ml as the limit of detection (l.o.d), using the criterion of l.o.d as the concentration giving a signal value three times that of the standard deviation.

Under constant deposition time of 5 min, the peak current varied with concentration of Hg(II). The plot of the peak current against Hg(II) concentration was linear only in a short range, after which the peak current levelled off rather rapidly (Fig. 7). The short time by which the saturation could be reached again suggesting easy access of Hg(II) ions to the polymer film. This mechanism of the Hg(II)–polymer binding process is not yet clear at this moment. The complex could probably be formed through the coordination of the Hg(II) ion involving the carbonyl groups of the amide linkages and the tertiary nitrogens in the piperazine moieties, similar to that proposed for the Cu(II) complex [28].

CONCLUSION

Poly(*N*-acryloyl-*N*′-methylpiperazine-co-methyl methacrylate) was synthesized by free radical polymerization. The monomer ratio in the copolymer was analyzed by FTIR spectroscopy. The copolymer film, attached to a glassy carbon electrode, could be used for the detection of Hg(II) ions in aqueous solution. The advantage of using the polymer film studied was that, unlike most of the other polymeric matrices, it required no doping of a modifier. In addition, the copolymer swelled in aqueous solution, allowing rapid access of Hg(II) ions for binding. Although the detection limit was not outstanding and the linear range of detection was relatively short, the potential application of this type of polymeric materials in CME for the detection of Hg(II) ion has been demonstrated.

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