Poly(*O*-methoxyaniline) Thin Films: Cyclic Voltammetry Study

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ABSTRACT: Electrochemical polymerization of poly(*O*-methoxyaniline) (POMA) thin films was carried out under cyclic voltammetric conditions. The cyclic voltammograms (CV) of the POMA films in the presence and absence of monomer in the aqueous solution of $1M$ H_2SO_4 were studied. The electrochemical degradation of the POMA films was investigated by cyclic voltammetry and UV-visible spectroscopy. It was observed that the rate of degradation is strongly dependent on the applied potential. UV-visible spectroscopy revealed no significant chemical modification or phase change from the degradation. The temperature dependence of the voltammetric response of the POMA films in the aqueous solution of $1M$ H_2SO_4 was also investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3009–3015, 1999

Key words: poly(*O*-methoxyaniline); electrochemical synthesis; cyclic voltammetry; electrochemical degradation; optical absorption

INTRODUCTION

In recent years, considerable attention has been given to the investigation of the basic features of the electrochemical synthesis and behavior of conducting polymer films because of their numerous potential technological applications in diversified areas.[1–4] However, it has now become apparent that variations in the process variables such as monomer concentration, supporting electrolyte, solvents, pH of the electrolyte, synthesis temperature, nature of the substrate, and so forth, result in the remarkable changes in the properties of conducting polymer films. Considerable efforts[5,6] have been made to study the influence of process variables on the electrochemical polymerization and redox reactions of various conducting polymers such as polyaniline, polypyrrole, and polythiophene. Several derivatives of these conducting polymers have gained the interest of researchers during the last couple of years with a view to explore the possibility of utilizing them as alternatives to the parent one.[7,8] Ocon and coworkers[7] have examined the surface characteristics of electrochemically synthesized poly(*O*-methylaniline) (POMA) films on polyfaceted gold single crystals using the scanning tunneling microscopy technique. More recently, Mattoso et al.[8] have studied the chemical synthesis of methyl, methoxy, and ethoxy ortho substituted polyanilines using a potential profile technique. The influence of monomer concentration, the surface resistance of the substrate, and the thermal properties of galvanostatically synthesized poly(*O*-anisidine) films was reported by Bedekar et al.[9] Lacroix et al.[10] have shown that the electropolymerization of methoxy substituted anilines is sensitive to the substituent position but not to the nature of the electrode. Although few attempts[8–10] have been made to investigate the electrochemical synthesis and properties of POMA thin films, the cyclic voltammetric investigations and electrochemical degradation of POMA thin films have not yet been studied.

In this article we report on the cyclic voltammetric investigations of electrochemically synthesized POMA thin films and the electrochemical degradation of these films in an aqueous solution of $1M$ H_2SO_4.

EXPERIMENTAL

The OMA monomer was double distilled before use. The transparent conducting SnO_2 : F (sheet resistance $\sim$ 20 Ω/cm) coated glass substrates were prepared using an indigenous spray pyrolysis system. The POMA thin films were synthesized electrochemically at room temperature under cyclic voltammetric conditions in a solution containing $0.1M$ OMA and $1M$ H_2SO_4 at a scan rate of 20 mV/s between -400 and 700 mV versus a saturated calomel electrode (SCE). A detailed description of the synthesis of POMA films is given elsewhere.[11] After 13 cycles the working electrodes were held at 600 mV until the current decayed to zero. Then they were removed from the electrolyte and washed with the supporting electrolyte solution. At least four POMA films were deposited under each experimental condition. The degradation of POMA films was studied by recording the cyclic voltammograms (CVs) in the potential range between -400 and 700 mV after holding at 700 and 400 mV (vs. SCE) for different time intervals in an aqueous solution of $1M$ H_2SO_4. For each time interval an identical freshly prepared POMA film was used for the degradation study. The optical absorption studies of these films were carried out *ex situ* using a microprocessor controlled double beam UV-visible spectrophotometer (Hitachi model U 2000). All the spectra were recorded at room temperature in the wavelength range of 300–1100 nm. Baseline correction was done before recording the spectra.

RESULTS AND DISCUSSION

CV of POMA Films

Figure 1 shows CVs recorded during the synthesis of POMA films at room temperature. The room temperature was measured during the synthesis and it was observed to be 27°C. In the present studies the switching potential was chosen to keep the oxidation current density at a low value. The CVs are very similar to those reported by Lacroix et al.[10] In the first positive cycle [Fig.
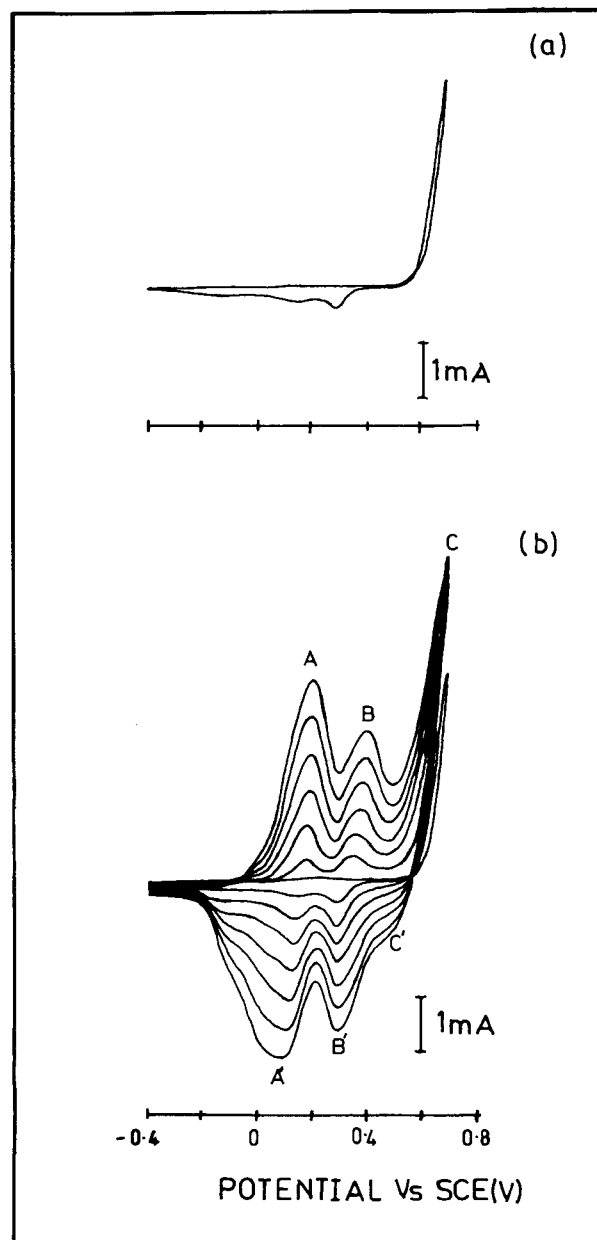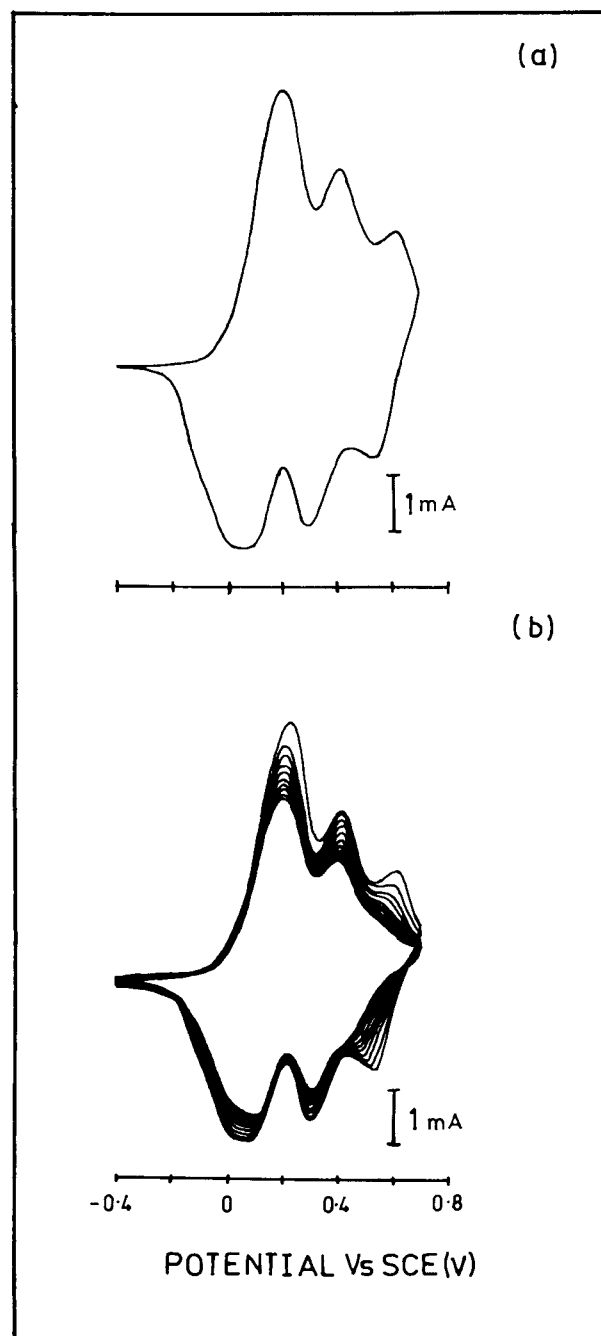

Figure 1 Cyclic voltammogram recorded during the synthesis of POMA films at a scan rate of 20 mV/s: (a) first scan and (b) scans recorded after every alternate scan.

1(a)] there is little oxidation until the potential is greater than 500 mV, and beyond this potential high anodic currents flow. The appearance of a peak at +260 mV during the first negative cycle was due to reduction of an anodically formed species. On repetitive cycling, three anodic peaks at 200 (peak A), 400 (peak B), and 700 mV (peak C) versus the SCE were observed. The redox peak

currents gradually increased with the number of cycles, indicating the growth of a conducting polymer film. The oxidation peaks were relatively sharper than the reduction peaks. It is known that these redox peaks are responsible for the change in the conductivity of POMA films: oxidation produces a conducting film and reduction produces an insulating film. Further, we observed that the reduction currents were smaller and the oxidation currents were higher. This observation is consistent with the transition from an insulator to a conductor.

To discriminate the origin of the different peaks, the voltammogram of the POMA film was recorded in an aqueous solution of $1M$ H_2SO_4. The CV [Fig. 2(a)] shows the appearance of only peaks A, B, A′, and B′ with the ratio of anodic to cathodic charge equal to one. Peak C was not observed in this case. It is obvious that in $1M$ H_2SO_4 a peak corresponding to the monomer oxidation cannot be observed. Indeed, the observed CV is in agreement with this fact and therefore peak C is attributed to the oxidation of the OMA monomer and hence the actual polymerization of the OMA monomer. It is known from the polymerization mechanism that the oxidation and polymerization processes are correlated. The anodic peak A is assigned to the oxidation of POMA deposited at the electrode surface, corresponding to conversion of amine units into radical cations.[12] It is well known[13] that the total polymer deposit at the electrode surface is proportional to the anodic current density at 200 mV. In polyaniline synthesis many researchers[12,13] have attributed the middle peaks in CVs to the presence of degradation products and observed that these peaks can be eliminated by controlling the potential limits and effectively the current density during the synthesis. However, in the present work it was not possible to avoid the middle peak (at 400 mV), even if the potential scan was cycled between −400 and 550 mV as shown in Figure 3. Therefore, in the present case the middle peak is not completely similar to that of polyaniline. This is in agreement with the results of Lacroix et al.[10] who attributed the middle peak in the CV of POMA to the greater ratio of non-para couplings to para couplings of the polymer. Further, observe from the inset of Figure 3 that the redox peak currents are fairly well proportioned to the scan rate, which suggests that the redox reaction is quite reversible.

The optical absorption spectrum of the as-deposited POMA film is shown in Figure 4. It indi-

Figure 2 Cyclic voltammogram of POMA films recorded in an aqueous solution of $1M$ H_2SO_4 at a scan rate of 20 mV/s: (a) first scan and (b) first 10 successive scans.

cates a major peak at ∼ 800 nm and a shoulder at ∼ 440 nm. The peak at 800 nm corresponds to the emeraldine salt (ES) form of POMA, while the latter may be attributed to the formation of radical cations.[14,15] The general features of this spectrum closely resemble those reported by Bedekar
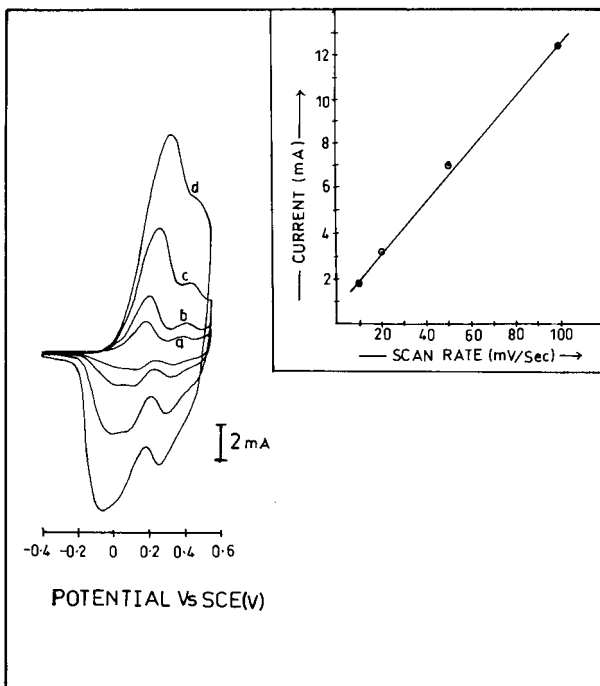
Figure 3 Cyclic voltammograms of POMA films recorded in an aqueous solution of $1M$ H_2SO_4 at scan rate of (a) 10, (b) 20, (c) 50, and (d) 100 mV/s. The inset shows the plot of the redox peak current against scan rate.

et al.[9] However, in our case the optical spectrum shows a shift in the peak position toward lower wavelengths, which may be attributed to the effect of the supporting electrolyte (H_2SO_4).

The multisweep voltammogram of the POMA film in $1M$ H_2SO_4 is shown in Figure 2(b). We observed that repeated scanning under the same experimental conditions only results in a slight decrease in the redox peak currents, indicating the fairly good electrochemical stability of POMA films in the potential range between -400 and 700 mV. The optical absorption spectrum (Fig. 4) of the film after the scans in $1M$ H_2SO_4 in the absence of monomer is identical to the spectrum of as-deposited POMA films, except the absorbance in the wavelength region of 450–650 nm is found to increase. The overall features of the spectrum clearly suggest that the stability of the film is fairly good, which is in agreement with the observed CV.

Electrochemical Degradation of POMA Films

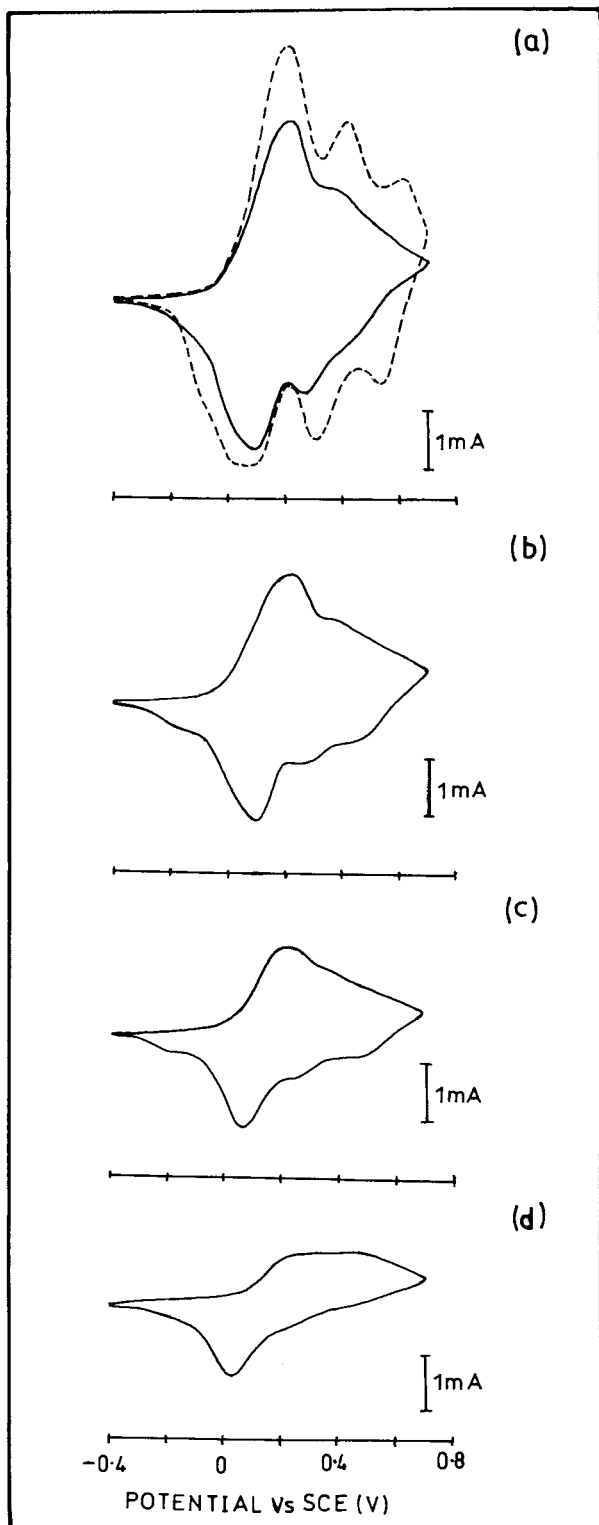Figure 5 shows the CVs of the POMA films recorded before and after prepolarization at 700 mV

(vs. the SCE) for different time intervals in an aqueous solution of $1M$ H_2SO_4. (The CVs for the prepolarization at 400 mV are not shown here.) In the absence of the prepolarization, the POMA film shows a stable CV. As the prepolarization time was increased, the redox peak at 200 mV diminished and a broad redox peak appeared at 500 mV. These observations are consistent with the reported degradation behavior of polyaniline films.[16,17]

The level of degradation was monitored in terms of the ratio of the discharge capacity after the degradation to that of the initial state, which is known as charge retention. The time dependence of the charge retention is the measure of the rate of degradation and is shown in Figure 6. We observed that the rate of degradation was faster at 700 mV but the film was quite stable at 400 mV, which is the peak potential of the second redox process. Therefore, it can be said that the POMA films are stable in the second redox peak potential region in the CVs.

The optical absorption spectra of the POMA films before and after the prepolarization at 700
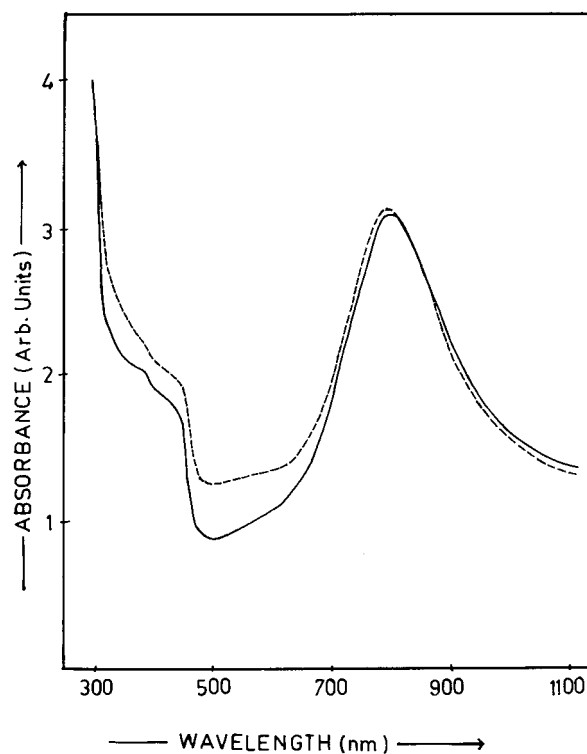
Figure 4 Optical absorption spectra of POMA films synthesized under cyclic voltammetric conditions (—) as-deposited and (---) after 10 cycles in an aqueous solution of $1M$ H_2SO_4.

Figure 5 Cyclic voltammograms (CVs) of POMA films recorded in an aqueous solution of 1M H$_2$SO$_4$ at scan rate of 20 mV/s after the prepolarization at 700 mV (vs. SCE) for (a) 15, (b) 30, (c) 120, and (d) 240 min. (· · ·) The CV before the prepolarization is also shown.
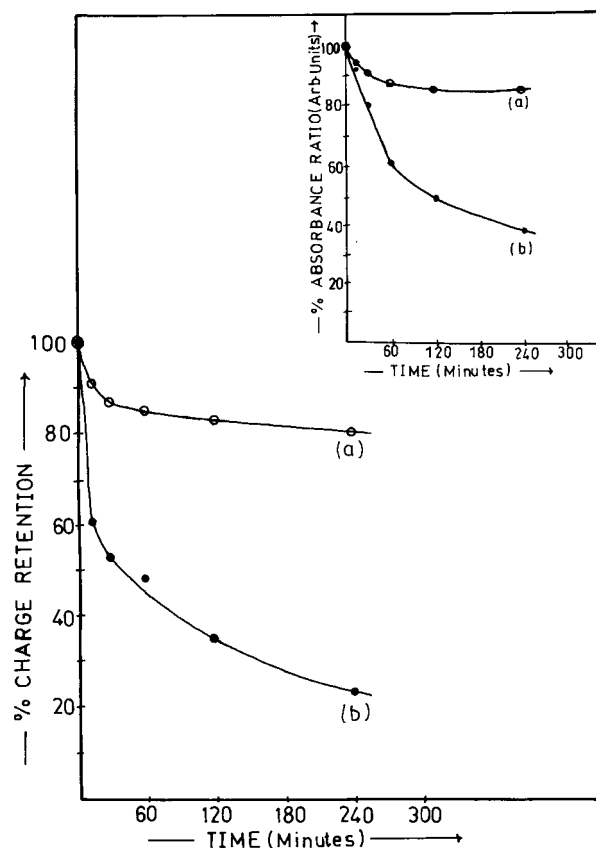
Figure 6 Variation of charge retention and the ratio of optical absorbance at 800 nm (inset) with the duration of prepolarization at (a) 400 and (b) 700 mV vs. SCE.
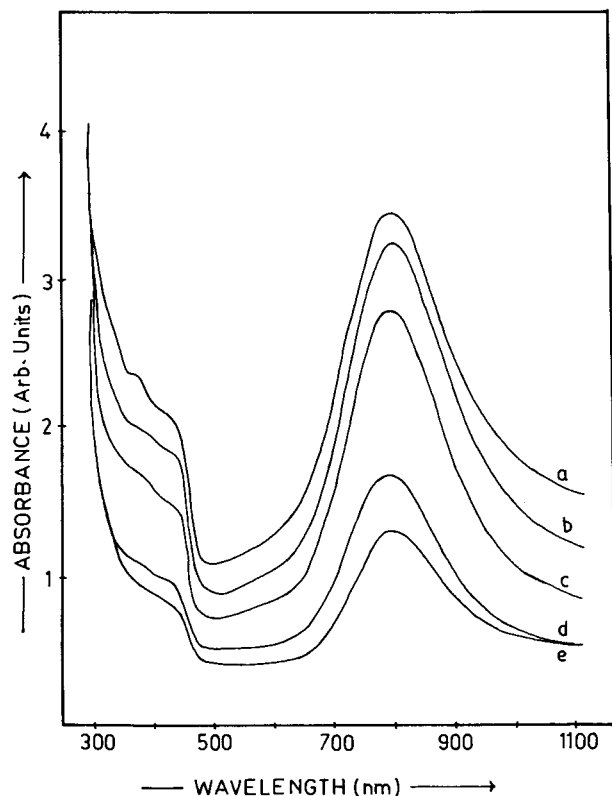
mV for different time intervals are shown in Figure 7. The shape and the overall features of the absorption spectra are identical. Therefore, it is reasonable to believe that no phase change or chemical modification occurred during the degradation. However, the total absorbance level rapidly decreased with the prepolarization time. Also, the green color of the film became less intense with the prepolarization time. These observations may possibly be due to the diffusion of the degradation products of POMA into the electrolyte and hence the decrease in the mass of the deposited POMA. The variation of the ratio of absorbance at 800 nm after the degradation to that of the as-deposited case as a function of the duration of degradation is shown in the inset in Figure 6. It is apparent that the conducting ES phase of POMA is fairly stable after the prepolarization at 400 mV. However, at 700 mV a rapid decrease in the absorbance ratio suggests that the ES phase of POMA degrades at a relatively faster rate. These observations support the CV results.

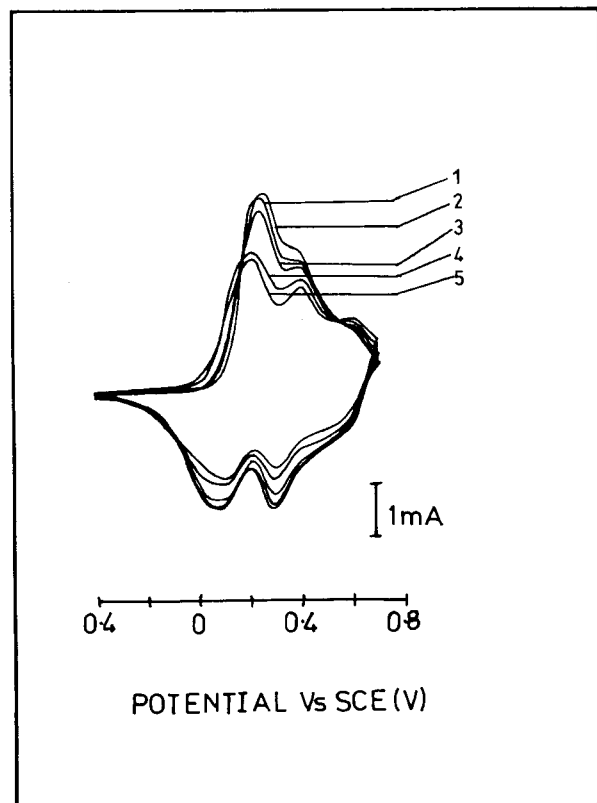**Effect of Temperature on Voltammetric Response of POMA Films**

Figure 8 shows the voltammetric response of POMA films in an aqueous solution of $1M$ H_2SO_4 at various temperatures between -6 and $40°C$. It is clearly seen that the redox peak positions are practically unaffected by temperature and the peak currents show a decrease at 27 and 40°C. Therefore, it can be said that there was no significant effect of temperature on the electrochemical behavior of POMA films. However, the charge retention capacity decreased at 27 and 40°C, which indicates that the film stability decreases with an increase in the temperature. To gain further understanding, detailed investigations are in progress on the effect of temperature and the pH of the electrolyte on electrochemical behavior.

CONCLUSIONS

The electrochemical synthesis of POMA films was carried out under cyclic voltammetric conditions.

Figure 8 Cyclic voltammograms of POMA films recorded in an aqueous solution of $1M$ H_2SO_4 at a scan rate of 20 mV/s at (1) -6, (2) 0, (3) 15, (4) 27 (room temperature), and (5) 40°C.

The optical absorption studies revealed the formation of a conducting ES phase. The CV of the POMA film was examined in an aqueous solution of $1M$ H_2SO_4. We found that the middle peak in the CV was not completely similar to that of polyaniline and the redox reaction was quite reversible. The electrochemical degradation was observed to strongly depend on the applied potential. UV-visible spectroscopy revealed no phase change or chemical modification of the POMA films during electrochemical degradation. The cyclic voltammetric response of POMA films was practically unaffected by the temperature.

Figure 7 Optical absorption spectra of POMA films synthesized under cyclic voltammetric conditions (a) before prepolarization and after the prepolarization at 700 mV (vs. SCE) for (b) 15, (c) 30, (d) 120, and (e) 240 min.

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