Bull. Mater. Sci., Vol. 26, No. 3, April 2003, pp. 329–334. © Indian Academy of Sciences.

Electrochemical synthesis and characterization of chloride doped polyaniline

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MS received 3 September 2002; revised 2 January 2003

Abstract. **Chloride doped polyaniline conducting polymer films have been prepared in a protic acid medium (HCl) by potentiodynamic method in an electrochemical cell and studied by cyclic voltammetry and FTIR techniques. The FTIR spectra confirmed Cl^- ion doping in the polymers. The polymerization rate was found to increase with increasing concentration of aniline monomer. But the films obtained at high monomer concentration were rough having a nonuniform flaky polyaniline distribution. Results showed that the polymerization rate did not increase beyond a critical HCl concentration. Cyclic voltammetry suggested that, the oxidation-reduction current increased with an increase in scan rate and that the undoped polyaniline films were not hygroscopic whereas chloride doped polyaniline films were found to be highly hygroscopic.**

Keywords. **Conducting polymer; electrochemical synthesis; polyaniline; cyclic voltammetry; FTIR.**

1. Introduction

Research in electroactive polymers, particularly in aromatic conducting polymers, has received considerable attention worldwide in the past few years because of their potential applications in the fields of microelectronics, optics and optoelectronics (Bernard *et al* 1998, 2001; Schultze *et al* 1999; Mousty *et al* 2001). Among these polymers, polyaniline (PAni) is one of the most widely studied conducting polymers because of its good conductivity that can be influenced both by the charging level and degree of protonation, its well defined electrochemical (redox) response, easy preparation and possible applications in rechargeable batteries, corrosion protection, light emitting diodes, molecular sensors, electrochromic devices and microwave screening (Inzelt *et al* 2001). Polyaniline is not charge conjugation symmetric, i.e. the valence and conduction bands are asymmetric to a great extent (Ghos *et al* 2001). A partial oxidation of PAni usually leads to the reorganization of bonds, resulting in an increase in electronic conductivity. The physicochemical properties of PAni are strongly related to the proportion of aryl amine and quinone imine units present (Genies *et al* 1988). PAni possesses two voltammetric redox pairs including three stable oxidation states, with the half-oxidized state (emaraldine) being highly conductive in its protonated state. Existence of different oxidation states of PAni makes it useful as an electrode material in electrochemical capacitors (Roβberg *et al* 1998; Fusalba *et al* 2001; Hu and Chu 2000, 2001).

In the present study polyaniline films have been prepared by electropolymerization from an electrolyte containing HCl and aniline monomer at different concentration ratios. The polymer films have been studied by cyclic voltammetry. FTIR spectra have been recorded for confirmation of Cl^- ion doping of the polymer films.

2. Experimental

Aniline (SRL, India) was distilled under reduced pressure and stored in darkness before use. As received HCl (Qualigens, India) and purified double distilled water were used in preparing the electrolyte solution. An electrochemical cell consisting of working and secondary electrodes of stainless steel was used. Saturated calomel electrode (SCE) was used as reference electrode. The electrolyte consisted of an aqueous solution of aniline monomer and acid HCl. Polymerization was carried out potentiodynamically using a potentiostate/galvanostate [Analytical Electrochemical Workstation, AEW2, Sycopel Scientific Ltd.]. Three samples were prepared from baths containing monomer concentrations of 0·05 M, 0·1 M and 0·15 M, respectively keeping the acid concentration fixed at 1 M and three samples were prepared with three different acid concentrations of 0·5 M, 1·5 M and 2·0 M at constant monomer concentration of 0·1 M. The deposition was carried up to 40 cycles at a scan rate of 25 mV/s. The potential was varied between – 100 mV and 1400 mV for deposition as well as for cyclic voltammetry experiments. Cyclic voltammograms of the polymers were recorded at scanning rates of 10, 20, 40 and 50 mV/s. Electrical conductivity has been measured by LCR

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Hitester Hioki model 3532–50. The FTIR spectra of the polyaniline samples have been taken by using Nicolet Impact 410 FTIR spectrophotometer.

3. Results and discussion

3.1 *Electrochemical deposition of polyaniline*

Depositions of the polymer films were carried out electrochemically by varying the monomer as well as acid concentrations. The deposition yielded a deep green film of polyaniline. Steps involved in the possible mechanism of the oxidative electropolymerization of aniline to polyaniline are given in figure 1. The polymerization takes place by oxidation at 1·0–1·2 V while potential is increasing followed by a de-protonation at 0·6–0·2 V in the reverse direction of potential. At lower monomer concentrations of 0·05 M and 0·1 M of aniline, the deposited films exhibit a smooth surface, uniform distribution and good adhesion to the electrode though the polymerization rate (i.e. the deposition current) is low. Figure 2 is the plot of deposition current (a measure of polymerization rate) as a function of monomer concentration. The figure shows that polymerization rate increases monotonically with monomer concentration and that at 0·15 M aniline concentration, the polymerization rate (deposition current) is quite high, but the film obtained has a rough surface, is flaky and shows poor adhesion. This may be

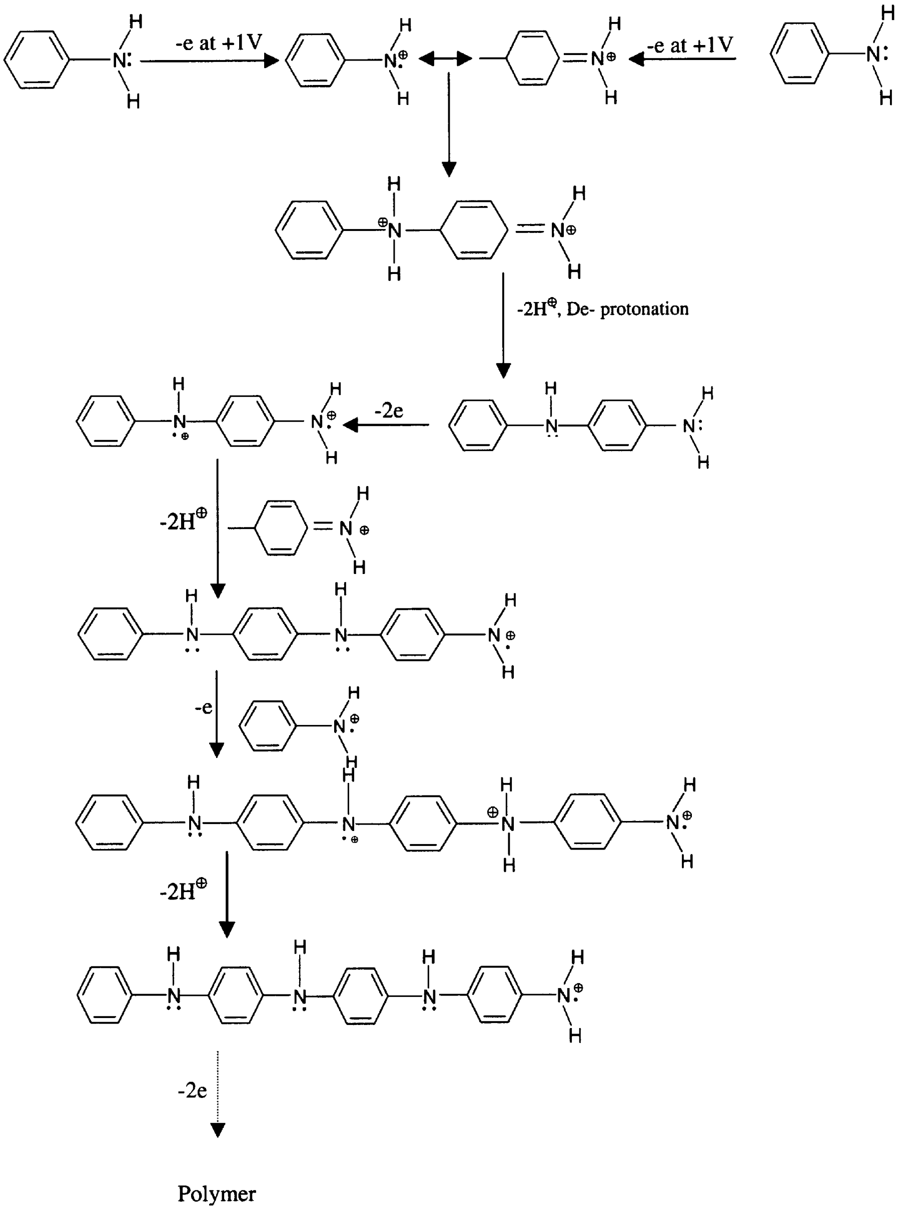

Figure 1. Mechanism of oxidative electropolymerization of aniline.

attributed to the faster rate of polymerization due to higher monomer concentration which does not provide time for polymer chains to stick smoothly on to the stainless steel electrodes. In table 1 are given the peak currents obtained in different cycles during polymerization at different monomer concentrations and 1·0 M HCl concentration. It is observed that the current in 5th cycle for 0·15 M monomer concentration is almost double to the current in 10th cycle for low monomer concentrations of 0·05 M and 0·1 M, which implies that the rate of polymerization for 0·15 M monomer concentration is roughly double to that for 0·05 M and 0·1 M monomer concentrations. These results suggest that even though the polymerization rate may be slower, but for improved adhesion and smooth and uniform films on stainless steel electrode the monomer concentration should be kept low (0·1 M).

The polymer films obtained by varying the acid concentration, however, do not show any notable change. The slow rate at low HCl concentration could be ascribed to lower proton concentration and hence lower protonation rate of the film. The rate of polymerization, however, does not increase monotonically with HCl concentration. Figure 3 shows that the deposition current gets saturated as HCl concentration exceeds 1·5 M, which implies that higher proton concentration cannot increase polymerization rate beyond a certain limit. The chloride ion (Cl^-) from the electrolyte enters the polymer film in the oxidative polymerization and remains in the polymer chain as dopant and contributes to oxidation/reduction by accepting/contributing one electron, which makes the polymer conducting. It is observed that the polymer films doped with chloride ion are hygroscopic and absorb moisture from air even if exposed to air for a very short period. However, undoped PAni films are not hygroscopic, and do not absorb moisture even if exposed to humid air for a long time.

3.2 *Cyclic voltammetry*

Figures 4a–c show cyclic voltammograms (CV) of the polyaniline films obtained at monomer concentrations 0·05 M, 0·1 M and 0·15 M, respectively in 1·0 M HCl at different scan rates (10, 20, 40 and 50 mV/s). Figures 5a–c show similarly the cyclic voltammograms of the polyaniline films recorded in 0·5 M, 1·5 M and 2·0 M HCl electrolytes, respectively containing a constant monomer concentration of 0·1 M. The cyclic voltammetry of polyaniline has been extensively discussed in the literature (Bernard *et al* 1998, 1999; Hatchett *et al* 1999; Rajendran *et al* 2000; Chen *et al* 2002; Schemid 2002). Voltammograms of the PAni at various scan rates can be differenti-

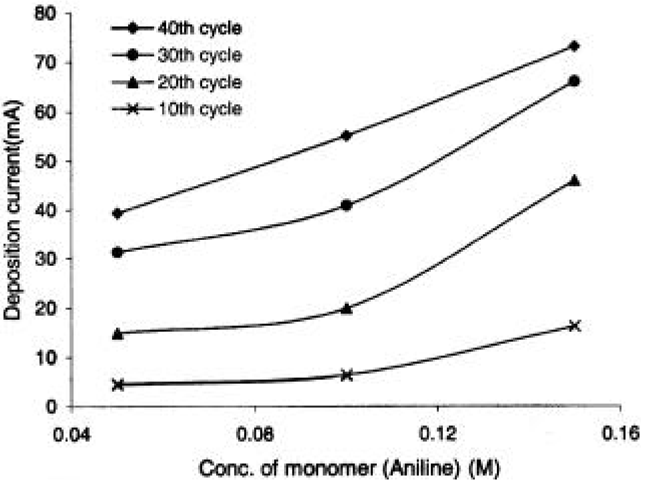

Figure 2. Monomer concentration vs deposition current showing a gradual increase in current with monomer concentration.

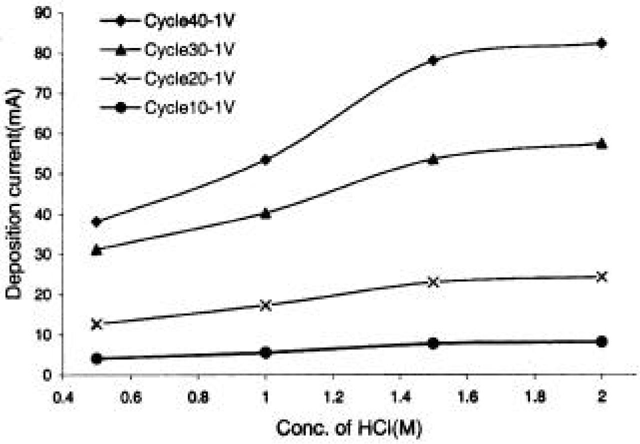

Figure 3. HCl concentration vs deposition current showing saturation at higher HCl concentration.

Table 1. Peak deposition current of different deposition cycles at constant HCl concentration and different monomer concentrations.

Monomer concentration (M)	Peak deposition current at 5th cycle (mA)	Peak deposition current at 10th cycle (mA)	Peak deposition current at 20th cycle (mA)	Peak deposition current at 30th cycle (mA)	Peak deposition current at 40th cycle (mA)
0·05	5·878	8·529	20·984	31·547	40·889
0·10	6·142	8·749	24·081	41·596	58·794
0·15	16·97	29·961	50·348	68·433	88·381

ated into three main regions. (i) 0·0 V to + 0·6 V is completely reduced state, (ii) from about 0·6 V to 0·9 V the PAni is in partially oxidized state and (iii) from about 0·9 V to 1·4 V it is in completely oxidized state. In figure 4c the reduction and de-protonation peaks are distinctly visible. In figure 4b the de-protonation peak is present but it is smaller than the reduction peak. In figure 4a, de-protonation peak is completely absent. The reduction peak for scan rate of 10 mV/s occurred at comparatively higher potential. In figures 5a–c also we can see separate reduction and deprotonation peaks at low scan rate (10 mV/s), but the peaks get diffused into a single peak at

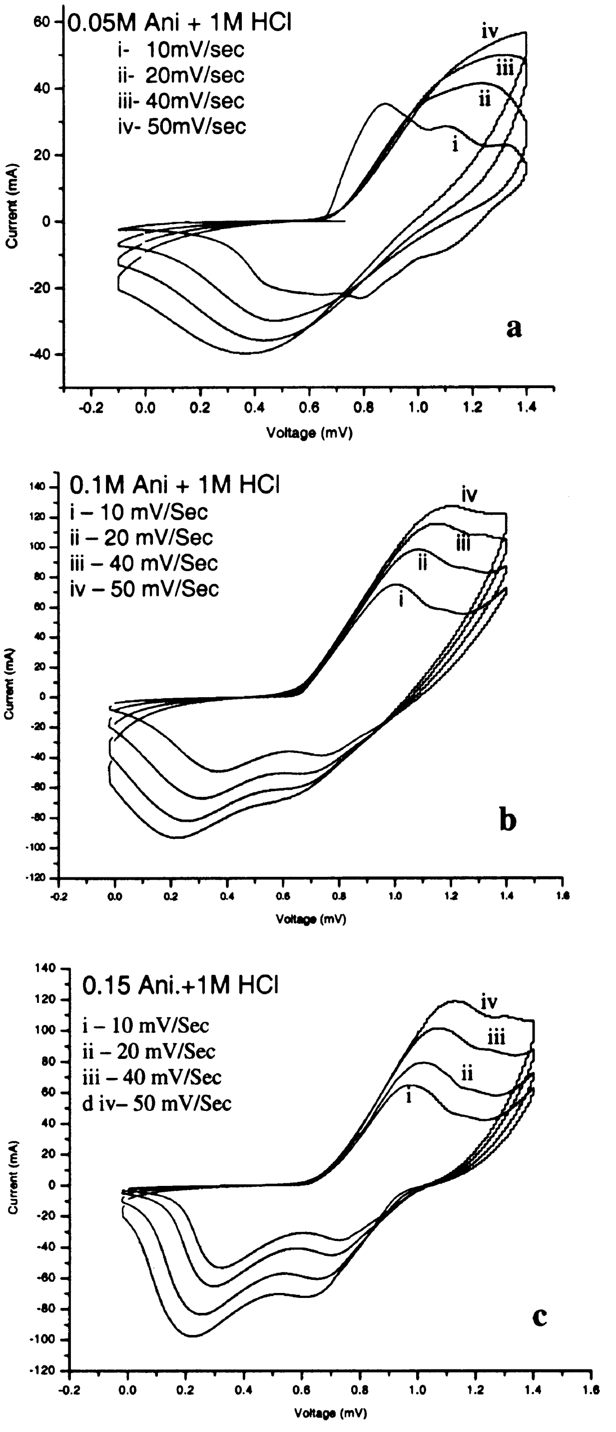

Figure 4. Cyclic voltammogram at different scan rates for (**a**) 0·05 M, (**b**) 0·1 M and (**c**) 0·15 M aniline in 1·0 M HCl.

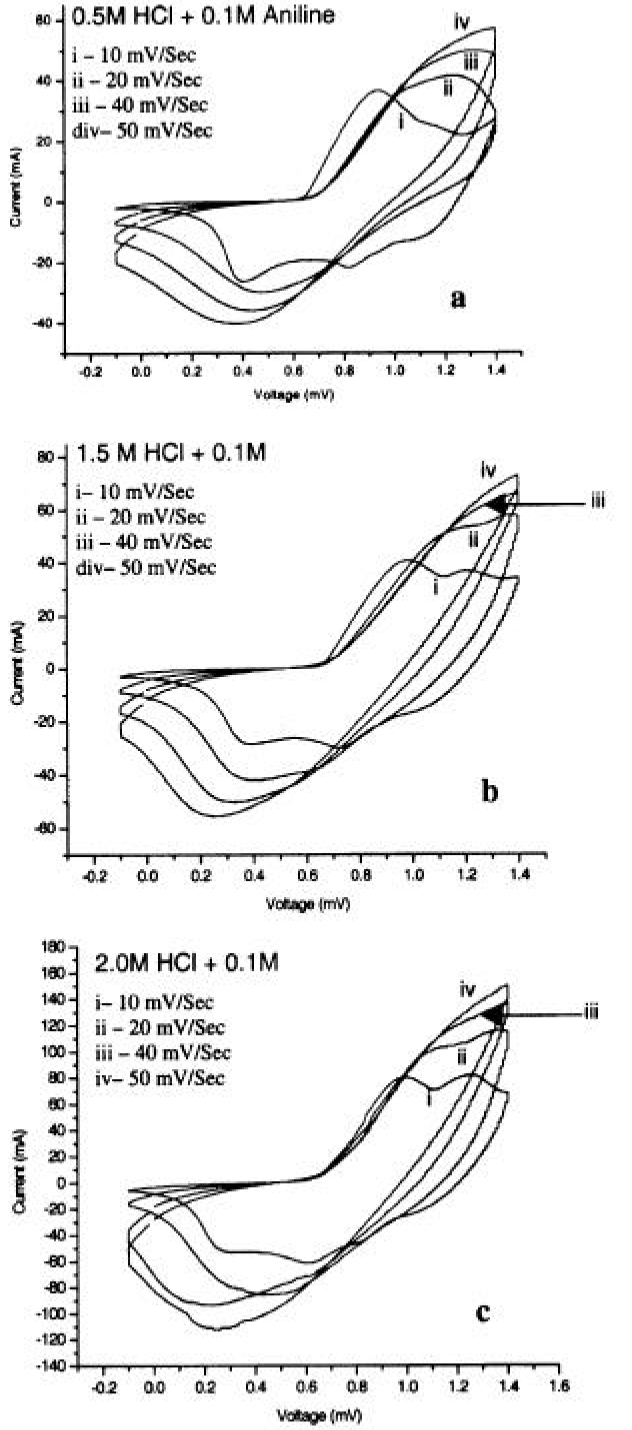

Figure 5. Cyclic voltammogram at different scan rates for 0·1 M aniline in (**a**) 0·5M, (**b**) 1·5 M and (**c**) 2·0 M HCl.

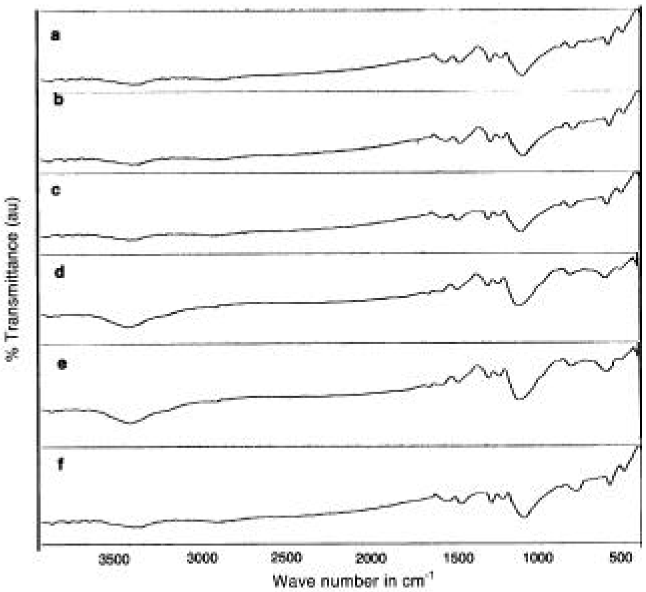

Figure 6. FTIR spectra of the polymer films (**a**) 0·05 M aniline, (**b**) 1·0 M aniline and (**c**) 1·5 M aniline in 1 M HCl and (**d**) 0·5 M, (**e**) 1·5 M and (**f**) 2·0 M HCl with 0·1 M aniline.

higher scan rates. From the cyclic voltammetry study we can say that both the cathodic and anodic currents are higher at higher acid concentration. This may be due to the increase in proton concentration in the electrolyte, which favours rapid protonation–deprotonation giving rise to larger currents. The colour of the PAni films changes from light green (bottle green) to deep green, which is also an indication of the oxidation-reduction taking place in the polymer electrode. The current density also increases/decreases in oxidation/reduction processes, more rapidly with the increase in scan rate. The oxidation peak for all the six films occurred in the region 1·0–1·2 V. Films of higher monomer concentration showed a little low oxidation peak near 1 V. The reduction and de-protonation peaks were found to lie in the range of 0·2–0·8 V. Interestingly no separate protonation peaks are observed in all the six samples. A broad peak, instead of two sharp peaks, one of protonation and the other of oxidation, is observed in our experiments. From these observations we conclude that the protonation and the oxidation are occurring at two very close potentials.

3.3 *Conductivity and FTIR spectroscopy*

The conductivity of the chloride doped and undoped polyaniline films are measured at room temperature (27°C) using LCR meter by two-probe method. The conductivity of the undoped films are of the order of 10^{-10} S/cm, whereas those of chloride doped films are of the order of 18–24 S/cm.

The FTIR spectra of polymer films obtained at constant HCl concentration of 1·0 M with changing monomer concentrations of 0·05 M, 0·1 M and 0·15 M are presented in figures 6a–c, respectively. Figures 6d–f show the FTIR spectra of polymers of constant monomer concentration, 0·1 M, with changing HCl concentrations, 0·5 M, 1·5 M and 2·0 M, respectively. The peak near 800 cm^{-1} is due to the N–H out-of-plane bending absorption. The strongest band observed near 1100 cm^{-1} and the band at 1235 cm^{-1} are due to C–C stretching and C–C twisting, respectively of the alkyl chain (Schemid *et al* 2002). The peak at 1300 cm^{-1} is due to the C–N stretching of the polymer. The C=C stretch absorption of aromatic compound generally occurs in the range of 1475–1600 cm^{-1}, in this study this peak was obtained at 1477 cm^{-1}. The peak due to N–H bending can be seen in the range of 1560–1640 cm^{-1}. The peak near 3000 cm^{-1} is due to the C–H stretching absorption. The stretching peak of N–H appeared in the range of 3420–3450 cm^{-1}. The C–Cl stretching peak arises in the range of 590–700 cm^{-1} (Koenig 1999; Pavia *et al* 2001). This confirmed the Cl^{-} doping of the electrochemically synthesized polyaniline films in HCl.

4. Conclusion

In the present work chloride doped polyaniline films have been directly prepared from an electrolyte containing HCl. The results show that for quality polyaniline films of smooth surface, better adhesion, less porosity and uniform distribution, the monomer concentration should be kept low (≈ 0·1 M), though the rate of polymerization is low at this concentration. At higher concentration, (0·15 M) of aniline, the rate of polymerization is high, but the film surface is rough, nonuniform, flaky and show poor adhesion to the electrode. It can also be concluded that the higher acid concentration does not lead to increase in the rate of polymerization beyond a certain limit. Cyclic voltammetry results show that oxidation of the polymer films occurs in the potential range of 1–1·2 V and the reduction occurs in the range of 0·2–0·8 V. FTIR spectra confirm the Cl^{-} ion doping in the polymer films.

Acknowledgements

We gratefully acknowledge UGC, New Delhi, for financial assistance (vide project no. F.10-53/2001 (SR-I). Help extended by Mr B Gohain, Department of Chemical Sciences, Tezpur University, in taking the FTIR spectra is also acknowledged.

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