

Poly(*m*-chloroaniline): Electrochemical Synthesis and Characterization

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ABSTRACT: The optical, morphological, thermal, and electrochemical properties of electrochemically synthesized poly(*m*-chloroaniline) reveal several unique features in comparison with similar well known properties of polyaniline. The nature and position of the halide substituent seem to be sensitive factor affecting the film properties. Optical spectra corresponding to different preparation conditions clearly display the significant role of pH during the formation of the conducting phase as gradual decrease in the ratio of absorbance at ~ 850 nm to that of simultaneously produced other oxidation state species obtained by decreasing the protonation level. These results are supported by the IR analysis of the samples. The relative intensity of quinoid to benzenoid ring modes [I_{1576}/I_{1470}] is highest at pH of -0.22 , and decreases with increasing pH of solution. Interestingly, with increasing pH from -0.22 to 3.3 , the morphology of the films show a transition from fibrillar to granular type. The thermal patterns exhibit a positive shift in the final decomposition temperature. The influence of pH of solution on the redox properties of the films is seen in terms of change in shape and current magnitude of cyclic voltammograms.

KEY WORDS Poly(*m*-chloroaniline) / Electrochemical Deposition / pH Effect / Optical Spectra / Morphology / Cyclic Voltammetry / Thermograms /

Commercial polyaniline and its substituted derivatives as perceived in an increasing number of diverse applications such as electrochromic devices, light weight batteries, etc., show these materials to be interesting and unusual π -conjugated conducting polymers.^{1–3} Most important conducting polymers can be produced by conventional electrochemical synthesis by anodic oxidation of monomer precursors,^{4,5} although their chemical stability varies drastically. In this regard, a large amount of work related to the synthesis and applications has been published especially on polyaniline.^{6–9} In comparison with polyaniline, the substituted analogues have received poor attention and more significantly the detailed electrochemical behavior of poly(*m*-chloroaniline) has not been studied adequately despite the possibility of shifting peak potentials by selecting the position of Cl substitution. No report is available demonstrating the formation of good quality poly(*m*-chloroaniline) films on suitable substrates for different promising applications. Indeed, it has been even reported that *m*-chloroaniline could not be polymerized efficiently to yield a film in protonic acid media like sulfuric and hydrochloric acids.¹⁰

Taking into consideration these aspects, the present paper mainly involves optimization of process parameters for electrochemical synthesis of good quality, adherent poly(*m*-chloroaniline) films in protic media. Further, the spectroscopic (optical and IR), morphological, thermal and redox properties of the generated films were investigated to illustrate the crucial role of pH during electropolymerization for controlling properties.

EXPERIMENTAL

All chemicals used were of analytical reagent grade. Electrolyte solutions of different pH (-1.66 , -0.22 , 0.47 , 2.18 , and 3.3) were prepared in doubly distilled

water by adding appropriate amount of hydrochloric acid to 0.1 M *m*-chloroaniline monomer solution. 5.85 g of sodium chloride was added as a supporting electrolyte to the solution (100 ml) containing lower concentration of hydrogen ions (pH 2.18 and 3.3). A one-compartment three-electrode system was used for depositing the polymer films where, $\text{SnO}_2:\text{F}$ coated glass (sheet resistance $10\ \Omega/\square$), calomel and platinum served as the working, reference and counter electrodes respectively. The details of preparation of $\text{SnO}_2:\text{F}$ coated glass electrodes by spray pyrolysis method have been reported elsewhere.¹¹

Poly(*m*-chloroaniline) films were galvanostatically deposited by applying various current strengths between 0.25 — 1.5 mA using a potentiostat/galvanostat (Model CL 95, Elico Pvt. Ltd., India). Well-adhered deposited films were washed, dried and subjected to characterization. Absorption spectra were monitored on a UV-Visible double beam spectrophotometer (Model Hitachi 220, Japan) in the range of 300 to 900 nm. Infrared spectra of the samples were recorded on a Perkin-Elmer [Model 1600] FT-IR spectrophotometer. The samples were prepared in pellet form using KBr and scanned between 400 to $4000\ \text{cm}^{-1}$. The optical micrographs were obtained from an optical microscope (Nikon HFX-DX Labhot-Pol) while, the thermograms of the samples were recorded on a thermogravimetric analyzer (Perkin-Elmer, Delta series Model 3700, U.S.A.) at a scanning rate of $10^\circ\text{C min}^{-1}$ in an O_2 atmosphere. Potential cycling was done in the range of -0.2 to 1.0 V vs. SCE at a scan rate of $100\ \text{mV s}^{-1}$ using a cyclic voltammetric instrument (Cypress Omni 90) consisting of potentiostat, function generator and recorder. The size of the working electrode for performing voltammetric experiment was kept fixed (3×3 mm) and all experiments were conducted at 25°C .

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RESULTS AND DISCUSSION

Spectroscopic Characterization

Optical

Figure 1 depicts the optical absorption spectra of poly(*m*-chloroaniline) films deposited as a function of pH of solution at different current strengths. From Figure 1, it appears that the polymerization of *m*-chloroaniline is a pH dependent process since different species are seen to be generated as a function of pH of the solution, establishing their identity at specific wavelengths. The film prepared from a solution of highly acidic pH of -0.22 shows characteristic spectra with a major peak at ~ 850 nm together with additional peaks appearing at ~ 660 and ~ 560 nm and a shoulder at ~ 440 nm representing the formation of conducting emeraldine salt phase, emeraldine base, pernigraniline base and radical cations respectively.^{12,13} On increasing pH of the solution to 0.47 the spectral features exhibit a transition in the absorption spectrum wherein, the peak at ~ 850 nm disappears completely while a new peak arises at ~ 760 nm apart from the other peaks observed in earlier case. A sharp intense peak at ~ 320 nm corresponding to leucoemeraldine phase is also noticeable at this pH. Further increase in pH to 2.18 and 3.3 yields films that are thicker and possess better quality in terms of smoothness and adherence in comparison with the films obtained at highly acidic pH as supported by the increase

in the magnitude of absorbance. Although the phases collected on the surface of electrode turn out to be identical with that obtained from solution at pH 0.47, the extent of sharpening in spectral features decreases gradually from pH 0.47 to 3.3. Examination of the results obtained by varying current strengths (Figure 1) reveals that there are no appreciable changes in the features of the absorption spectra of poly(*m*-chloroaniline) deposited galvanostatically at respective current strengths. Nevertheless, enhancement in the rate of reaction is seen in terms of magnitude of absorbance. The overall results of optical spectra of poly(*m*-chloroaniline) films suggest that highly acidic pH of solution (-0.22) containing 0.1 M monomer concentration favours the formation of greater fraction of the conducting emeraldine salt phase. In contrast, the deposition in the medium of pH of -1.66 does not produce adhering or smooth films and hence the spectral results are not recorded.

The above spectral features can be interpreted in the light of the mechanism of polymerization proposed earlier.¹⁴ The crucial step which hinders the polymerization process in the present case is the head to tail attack of the two radical cations leading to the formation of a dimer (RC-RC coupling). From our previous investigations on poly(*o*-anisidine),¹⁴ it is established that the formation of dimer *via* head to tail coupling is the most favoured process since $-\text{OCH}_3$ is an electron donating group ($-I$ or $+I$) and is a strong activator ($+R$

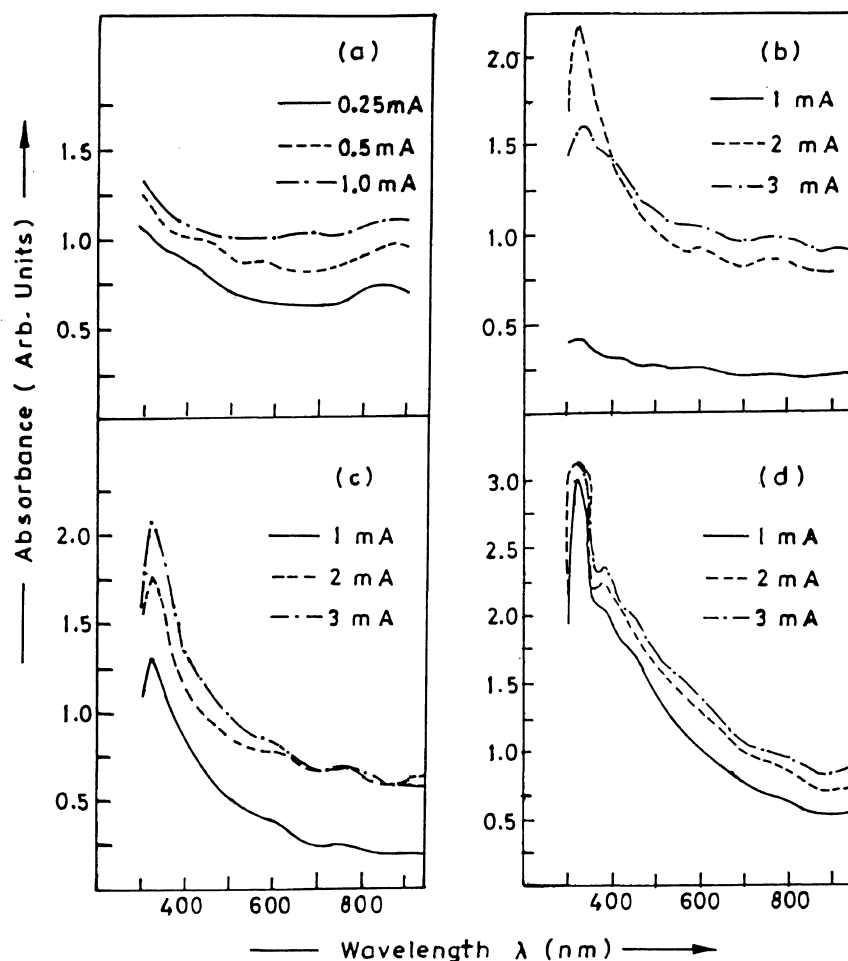
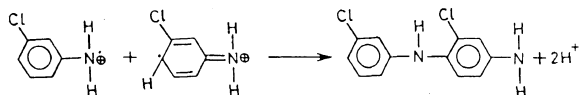


Figure 1. Optical absorption spectra of poly(*m*-chloroaniline) films deposited as a function of pH of the solution. (a) -0.22 ; (b) 0.47; (c) 2.18; (d) 3.3 (sheet resistance of electrode = $10 \Omega/\square$).

and $-R$) due to which electron is easily available for bonding.¹⁵ Contrary to this, Cl^- situated at *meta* position, in *m*-chloroaniline is strongly electron withdrawing, and access of electrons for bonding is presumably difficult as a result of which, the head to tail coupling of radical cations does not take place efficiently as in the case of poly(*o*-anisidine). This obviously restricts the formation of dimer which in turn limits the rate of polymerization.



The dimer formed in the above reaction undergoes oxidation generating the pernigraniline base of the polymer, which appears at a ~ 560 nm in the optical absorption spectra. At pH -0.22 , the pernigraniline base formed initially protonates into the pernigraniline salt, which on reduction, yields emeraldine salt proving its existence in terms of a broad peak around ~ 860 nm. At pH 0.47 , 2.18 , and 3.3 the conversion of base into salt form is inhibited and instead, it undergoes reduction and subsequently oxidizes the incoming monomer molecules to form lower oxidation state species (~ 660 nm, ~ 440 nm, and ~ 320 nm) as demonstrated in Figure 1b, c, and d.

The protonation of the pernigraniline base to salt in case of poly(*o*-anisidine) is inhibited due to the unavailability of protons particularly at solution pH of 2.18 .¹⁶ However, the present results show that the conversion of these two species does not take place even at pH of 0.47 indicating that these higher acidic conditions are required for complete protonation of poly(*m*-chloroaniline). The exact reason behind this is still not clear and further studies are necessary to confirm this possibility.

It is very essential at this stage to account for the competitive reactions that take place along with the polymerization reaction. These are especially important to explain the magnitude of absorbance as a function of pH of the solution. In highly acidic solution, even though the rate of deposition is high, the film deposited is relatively thin due to the formation of soluble oligomeric derivatives to a greater extent.¹⁷ At higher pH (2.18 and 3.3) the competitive reactions are inhibited with a simultaneous enhancement of the polymerization over other reactions, leading to the formation of thicker and good quality films. In conclusion, the earlier inconsistencies regarding the preparation of poly(*m*-chloroaniline) could be mainly explained due to the lack of pH control during synthesis.

IR Spectra

IR spectra of the films obtained by electrochemical oxidation of *m*-chloroaniline as a function of pH of solution are presented in Figure 2. The key band assignments are given in Table I and agree well with those reported by earlier workers.^{18–21} The band between 872 – 880 cm^{-1} observed in all samples is attributed to the paradisubstituted derivative of the benzene ring, indicative of polymer formation. Of particular interest are the bands in the vicinity of 1475 – 1600 cm^{-1} cor-

responding to benzenoid and quinoid, respectively. The presence of these bands clearly shows that the polymer is comprised of insulating (leucoemeraldine, emeraldine base, and pernigraniline) and conducting (emeraldine salt) phases. However, a comparison of relative intensities of the quinoid to benzenoid ring modes (I_{1576}/I_{1470}) shows that the ratio is highest at pH of -0.22 , which decreases with increasing pH of solution. Thus at highly acidic pH (-0.22 and 0.47) mixed phases (pernigraniline, emeraldine base, and emeraldine salt) may form predominantly. At higher pH of 2.18 and 3.3 the formation of a lower oxidized leucoemeraldine phase is favoured over any other higher oxidized state fragments.²¹ The results are in agreement with the optical spectra as per the above discussion. The bands observed at ~ 1286 and 1300 cm^{-1} represent C–N stretching vibrations. The band at 1120 cm^{-1} appears in plane C–H bending motion of aromatic rings, while the bands at 780 and 680 cm^{-1} represent out of plane C–H bending modes.

Morphological Characterization

The morphological characterization has been carried out to evaluate the overall quality of film in terms of uniformity and adherence particularly due to the effect of Cl^- in deciding the growth patterns. At pH -0.22 "flabellate type" (densely branched coiled fibres) texture is seen especially at lower magnification of $100\times$ covering the surface of electrode as a whole (Figure 3a). The interlinking of the fibres is distinctly observed at a higher magnification of $400\times$ (Figure 3b). The films deposited at pH 0.47 exhibit a combination of fibres and granules and randomly distributed fibres show splitting at the ends as depicted in Figure 3c. However, these fibres are thicker than at pH -0.22 . The granules scattered throughout the film also show their presence indicating loss in selectivity in obtaining the conducting phase of polymer. Although increase in pH to 2.18 and 3.3 show an exclusive granular type morphology, finer sized granules along with stillate shaped growth centres are observed for pH 2.18 (Figures 4a and b), whereas films deposited at pH 3.3 reveal granules with a variable size (Figure 4c).

The presence of fibres in the optical micrographs suggests that the Cl^- group present at the meta position does not cause steric hindrance to polymerization thereby permitting the growth of long chain fragments. The distinctly observed fibrillar morphology at pH -0.22 is obvious since at this pH, the conducting phase is formed in a greater fraction as compared to that at other pH. Nonuniformity with respect to length of fibres seen in the micrograph (Figure 3a) for the films deposited at pH -0.22 indicates the existence of other oxidation state species along with emeraldine salt. At pH 0.47 , in spite of the absence of a distinct peak in optical spectra corresponding to the emeraldine salt, short tiny fibres with granules are seen in the micrograph. This suggests that the polymer formed on the electrode surface still contains fractional contribution from the emeraldine salt phase. Contrary to this, formation of the insulating phases at pH 2.18 and 3.3 , respectively, show variable size granules. These results are in excellent agreement with spectral characterization as well as our previous results on poly(*o*-anisidine).¹⁶

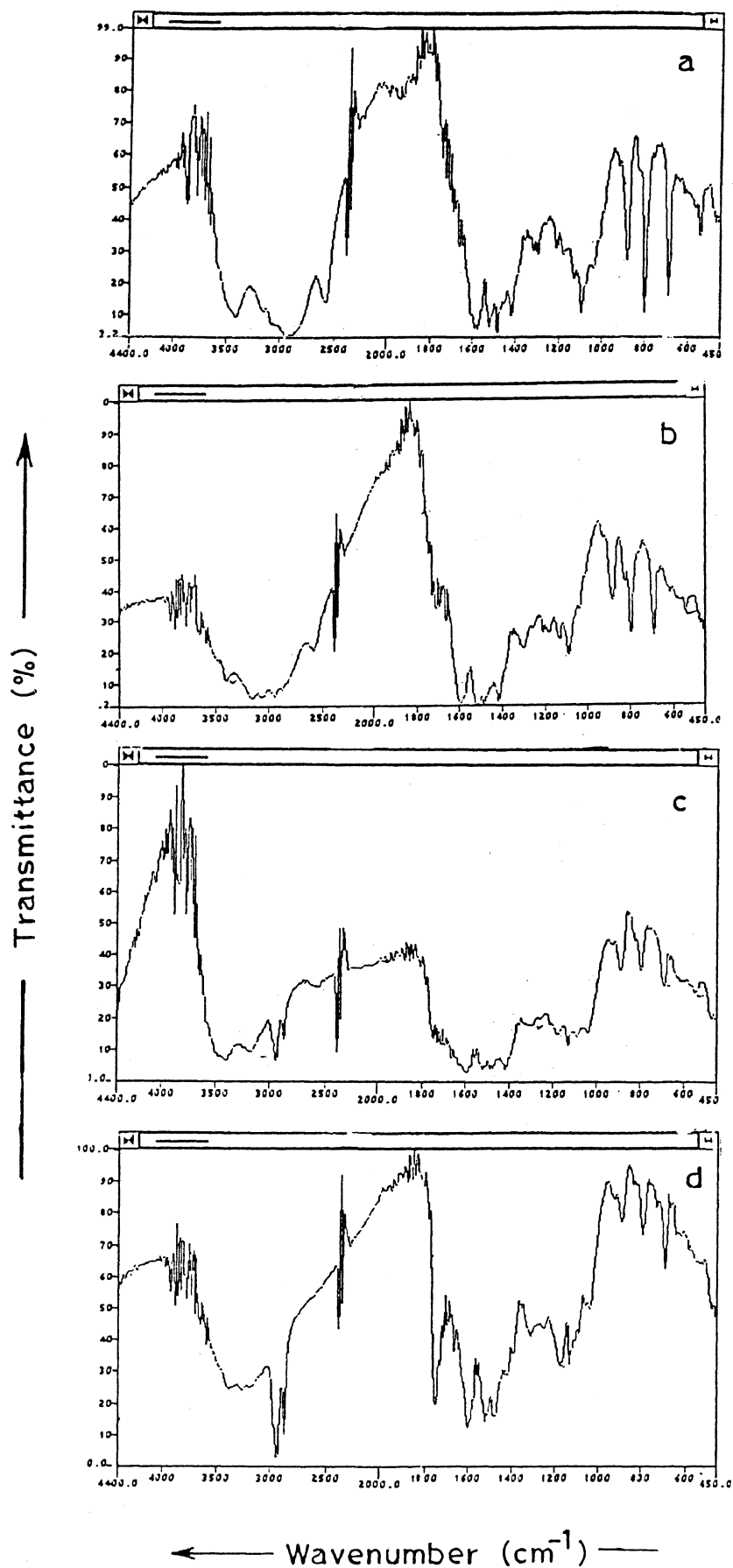


Figure 2. IR spectra of poly(*m*-chloroaniline) films deposited as a function of pH of solution. (a) -0.22; (b) 0.47; (c) 2.18; (d) 3.3 (sheet resistance of electrode = $10 \Omega/\square$).

Table I. Characteristic frequencies (cm^{-1}) obtained from IR spectra

pH	C_6 Ring symmetry		<i>para</i> -Disubstituted benzene ring/ cm^{-1}	In plane (C-H) bending cm^{-1}	$\nu(\text{C-H})$ cm^{-1}	$\gamma(\text{C-H})$ cm^{-1}	$\nu(\text{C-H})$ cm^{-1}	$\nu(\text{N-H})$ cm^{-1}
	Quinoid ring/ cm^{-1}	Benzenoid ring/ cm^{-1}						
-0.22	1576	1476	872	1108	2924	786	1284	3392
				1188	2394	676		
0.47	1582	1476	872	1122	2984	786	1286	3482
				1174	3046	676		
					3078			
					2394			
2.18	1586	1476	880	1120	2926	784	1334	3386
				1166	2854	680		
3.3	1590	1476	880	1120	2926	780	1300	3376
				1166	2854	682		

ν = stretching vibrations; γ = out of plane bending vibrations.

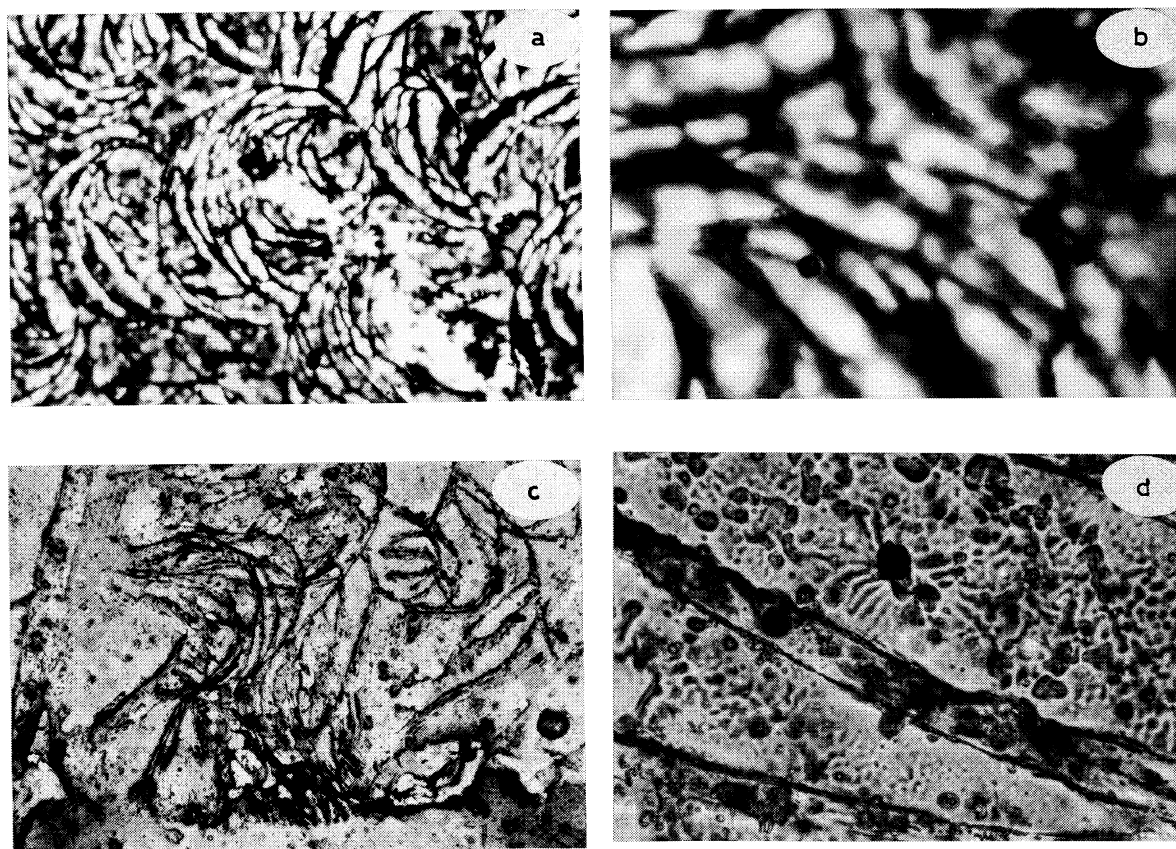


Figure 3. Optical micrographs of poly(*m*-chloroaniline) films deposited electrochemically as a function of pH of the solution. a) and b) pH = -0.22; c) and d) pH = 0.47 [magnification a) and c) 100 \times , b) and d) 400 \times , sheet resistance of electrode = 10 Ω/\square].

The important observation in the present case is that although variation in the morphology was observed by changing the protonation level, the growth of the polymer in all cases takes place *via* well defined growth channels (Figure 4a). When the conducting phase is generated during polymer deposition current density at the tip of these channels becomes high and as a result other molecules are attracted leading to the growth of fibre. If the depositing material is insulating in nature it coagulates and grows in size individually leading to granular morphology as observed in Figures 4b and c.

Thermal Characterization

Since different species are formed simultaneously at
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each pH as inferred from the optical and morphological results thermal studies were performed to understand the expected, but subtle changes in the decomposition patterns as a function of pH of solution. The thermograms obtained for the films deposited at different pH are presented in Figure 5. At highly acidic pH the thermogram follows a three step decomposition route where each step has its usual meaning²² corresponding to loss of H_2O molecules, volatilization of Cl^- as HCl and complete decomposition and degradation of the polymer matrix. Increase in pH to 0.47 and 2.18 during electropolymerization disturbs this generalized trend incorporating an additional step of weight loss prior to the decomposition arising due to the loss of low mo-

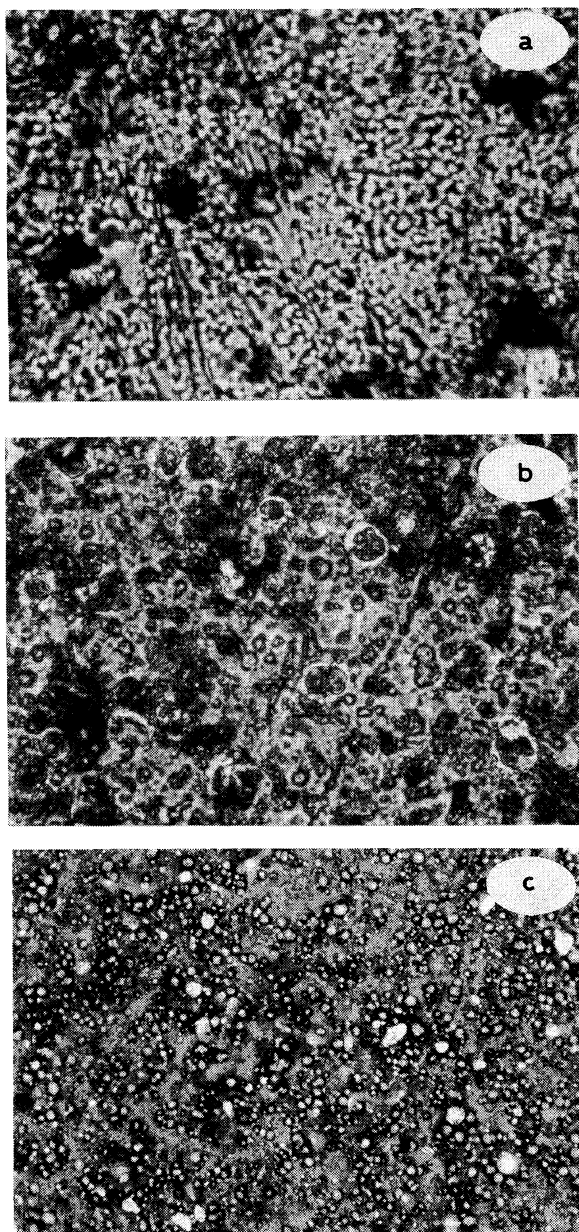


Figure 4. Optical micrographs of poly(*m*-chloroaniline) films deposited electrochemically as a function of pH of the solution. [a) and b) pH = 2.18; c) pH = 3.3 at magnification of 100 \times ; sheet resistance of electrode = 10 Ω/\square].

lecular weight fragments. Interestingly, loss in the second stage at these pH (0.47 and 2.18) is comparatively larger than that observed at pH -0.22 indicating loss of Cl⁻ preferably from short length oligomers. In addition to this, the fraction of high temperature decomposing fragments (fourth step) is found to be greater in this case. The disappearance of the initial step is observed for films deposited at pH 3.3, which may be due to the presence of predominant fraction of a non-ionic insulating phase. However, the rest of decomposition steps are identical to that for pH 2.18.

The above results display clear differentiation between the loss of Cl⁻ attached at *meta* position of benzene ring with that of the loss of chlorine attached to the polymer in the protonated phase in subsequent stages of decomposition. As noted from the optical spectra, at pH -0.22 the conducting phase is formed appreciably due

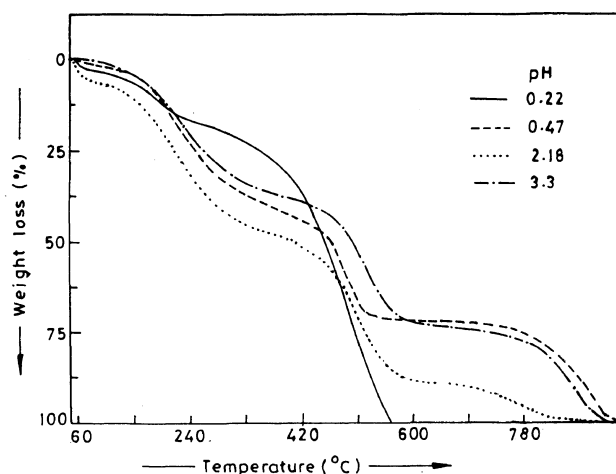


Figure 5. Thermograms of poly(*m*-chloroaniline) films deposited electrochemically as a function of pH of the solution. (sheet resistance of electrode = 10 Ω/\square ; current strength applied = 1 mA).

to which, protonated chlorine ions volatilize ($\sim 12.66\%$) in the region of 130–240°C. This loss seems equal to that for poly(*o*-anisidine) deposited electrochemically under identical condition.¹⁶ Therefore, it is concluded that the loss of benzenic Cl⁻ at pH -0.22 takes place in the beginning of the third stage, which is accompanied by destruction of the backbone completely. In contrast to this, at higher pH loss in the initial stage of second step can be attributed to the low molecular weight fragments along with a meagre amount of chlorine that could be coming from the fraction of pernigraniline salt. Further heating of the polymer leads to the loss of Cl⁻ present at *meta* position, wherein the chlorine may detach from the benzene ring and undergoes vaporization completely at around 400°C. Followed by this, the polymer backbone gets loose resulting in breakdown into several oligomers which can be clearly seen in the third stage of decomposition. This process slowly attains a steady state as indicated by a plateau in the thermogram. In the last step, stable products formed in plateau region degrade easily contributing towards complete weight loss of the polymer. The difference observed in the final stage of decomposition is attributed to the nature and degree of conjugation of the resulting species at each pH. The degree of conjugation is greater in insulating pernigraniline phase as compared to the lower oxidation state of emeraldine salt and as the amount of insulating phase increases in the film matrix, the decomposition temperature is seen to shift to a higher value upto 850°C.

Cyclic Voltammetric Studies

To understand the redox behavior of the electropolymerization of poly(*m*-chloroaniline) synthesized at various pH, cyclic voltammetric studies were conducted. Previous studies on poly(*o*-anisidine) have already demonstrated the capability of cyclic voltammetric technique in unraveling the important role of pH in determining the growth and phase formation during electropolymerization. The voltammograms (Figure 6) for poly(*m*-chloroaniline) clearly demonstrate the influence of hydrogen ion concentrations on the redox process in the system. pH dependent peak potentials corresponding to various species in cyclic voltammograms of

Table II. Variation in peak potentials (*vs.* SCE) with pH of different redox couple in the cyclic voltammograms of 0.1 M poly(*m*-chloroaniline) (scan rate = 100 mV s⁻¹; sheet resistance of electrode = 10 Ω/□)

pH	E_{Pa1} V	E_{Pc1} V	E_{Pa2} V	E_{Pc2} V	E_{Pa3} V	E_{Pc3} V	E_{Pa4} V	E_{Pc4} V	E_{Pa5} V	E_{Pc5} V	E_{Pa6} V	E_{Pc6} V
-1.66	—	-0.05	—	—	0.37	0.32	—	—	0.58	0.51	—	—
-0.22	—	—	0.13	0.09	0.35	0.32	—	—	0.56	0.50	—	—
2.18	—	-0.02	0.23	0.22	0.37	0.39	0.49	—	0.62	—	0.71	—
3.3	—	0.05	0.26	—	—	0.39	0.44	—	0.65	—	0.71	—

poly(*m*-chloroaniline) are recorded in Table II.

Voltammograms of poly(*m*-chloroaniline) films in the solution of pH -1.66 show two prominent redox peaks at 0.37 V and 0.57 V. The former can be attributed to the formation of benzidine derivatives along with a small fraction of emeraldine salt,²³ while latter to the presence of diradical dication.²⁴ The absence of peak around 0.13 V at -1.66 pH demonstrates the short term stability of radical cations in highly acidic solution, which is in agreement with our previous results on poly(*o*-anisidine).¹⁶

Increase in pH to -0.22 does not disturb the generalized pattern of cyclic voltammogram as observed at pH -1.66 except a new peak corresponding to the radical cation emerges around 0.13 V. Thus it can be stated that the concentration of protons at this pH is quite sufficient for making radical cation stable. However, the voltammogram obtained at pH 2.18 (Figure 6c) clearly reveals the presence of three peaks (~0.49, 0.62, and 0.71 V) on anodic side besides the two prominent redox couples at (~0.23 V and 0.37 V), respectively. The peak appearing at ~0.49 V indicates the formation of benzoquinone while the ~0.71 V corresponds to the presence of pernigraniline phase of the poly(*m*-chloroaniline).²⁴ The absence of cathodic peak ~0.62 V suggests that the amount of diradical dication formed during the polymerization immediately gets converted into the pernigraniline phase of polymer. The pernigraniline phase once formed autocatalyses the polymerization. On increasing the pH to 3.3 the cyclic voltammetric features are completely distorted (Figure 6d) so that the redox couples at 0.26 V and 0.44 V are barely discernible. However, the peak at ~0.37 V is absent revealing complete elimination of emeraldine salt along with benzidine derivatives. The attainment of limiting peak current value after 7th to 8th cycle additionally justifies the above statement. This observation matches well with that of the results reported for the optical spectra.

Apart from this, it is necessary to account for the charging current contribution to explain the sudden rise in the initial deposition current. This is especially important since substitution of Cl⁻ at the *meta* position drastically modifies the permselectivity of the polymeric film²⁵ and as a result, the incorporation of anions has been facilitated to larger extent as manifested by high charging current contribution. Although, it is difficult to see why the permselective properties of films are drastically affected by the *meta* substituted chlorine, a measurement of double layer capacitance may provide additional information and studies pertaining to this are essential to illustrate the mechanism completely. The high deposition current soon disappears in subsequent cycles

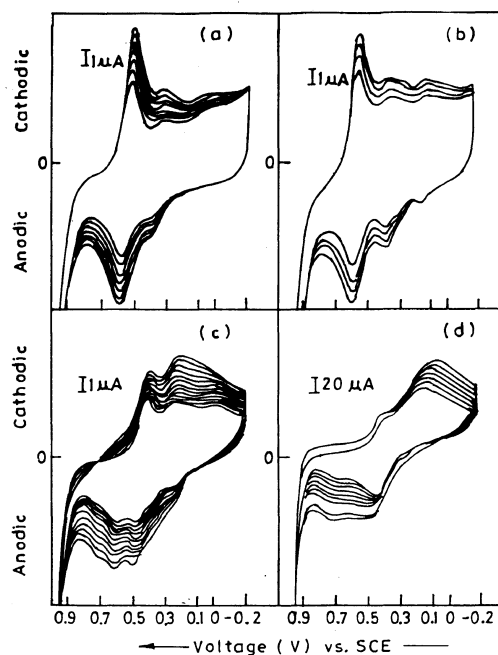


Figure 6. Cyclic voltammograms of poly(*m*-chloroaniline) films on substrates with a sheet resistance of 10 Ω/□ at a solution pH of a) -1.66, b) -0.22, c) 2.18, and d) 3.3 (scan rate 100 mV s⁻¹). Voltage is *vs.* SCE.

and growth continues mostly on the polymer surface irrespective of the pH of the solution.

To gain better understanding of the role of Cl⁻ situated at *meta* position, the cyclic voltammograms of poly(*m*-chloroaniline) are compared with that of polyaniline. The comparison of polyaniline and poly(*m*-chloroaniline) with respect to voltammograms at the same pH, monomer concentration and scan rate illustrates several interesting features (Figure 7). In particular, the electronic effect of *m*-chloroaniline substitution on various redox processes involving radical cation intermediates will be significant to control film properties. This is especially true since polymerization of aniline is well known to be pH dependent and require the acidic conditions.²⁶ More specifically, the enhanced acidity of *m*-chloroaniline (peak AA') confirms the crucial role of proton during initial process of polymerization, in complete agreement with the discussion outlined above.

Figure 7 shows the first peak of radical cation observed at 0.13 V in poly(*m*-chloroaniline) shifted 100 mV more positive for polyaniline. This accounts for the formation of radical cations as a thermodynamically more favoured process in polyaniline probably due to the presence of electron withdrawing Cl⁻ group. This is also confirmed when one compares the magnitude of current of both

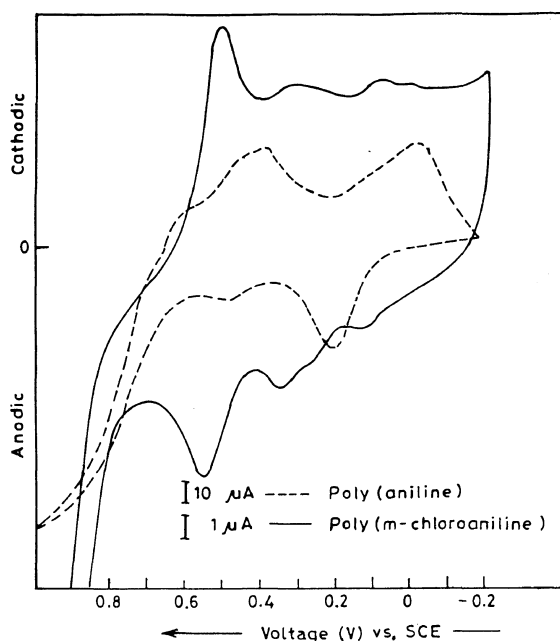


Figure 7. Comparative cyclic voltammograms of polyaniline and poly(*m*-chloroaniline) films taken under similar preparative condition using substrate resistance $10\ \Omega/\square$ at a solution pH of -0.22 . Voltage is vs. SCE.

the species whereby polyaniline exhibits current magnitude almost 10 times higher than that of poly(*m*-chloroaniline). The above observations also prove the formation of a greater fraction of emeraldine salt in polyaniline than that of poly(*m*-chloroaniline).

Drastic changes can be expected for peak CC' as it is known to be strongly pH dependent in comparison with the peak of radical cation. Since we have taken the first cycle for comparing polyaniline and poly(*m*-chloroaniline) the peak of diradical dication is absent in case of polyaniline. However, on further cycling this peak appears around 0.6 V and is 40 mV more positive than that of poly(*m*-chloroaniline). The peaks present at 0.24 V and 0.35 V correspond to intermediate species including soluble benzidine derivatives, while the peak at 0.49 V establishes the identity of benzoquinone in relatively smaller fraction in case of poly(*m*-chloroaniline).

CONCLUSIONS

A systematic investigation of the electropolymerization of poly(*m*-chloroaniline) in aqueous acid media indicates the importance of pH control in dictating various film properties including electrical conductivity, thermal stability, morphological, and redox properties. Although higher fraction of conducting phase is obtained at pH -0.22 , the film quality in terms of adhesion, thermal

stability, and appropriate morphology is found to be better for films prepared at higher pH. Comparison of these results with the electrochemical behavior of poly(*m*-chloroaniline) demonstrates the importance of Cl^- substitution in modifying the permselective and redox properties of these conducting polymers.

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