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Electrochemical synthesis and characterization of poly(m-toluidine)

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Poly(m-toluidine) was prepared by electrochemical polymerization of the corresponding monomer on gold and tin oxide electrodes, in acid medium. The polymer was characterized by elemental analysis, cyclic voltammetry, *I–t* curves and scanning electron microscopy. The utility of poly(m-toluidine) as an anion-exchange film is demonstrated on the basis of the electrostatic incorporation of anionic redox species into the poly(m-toluidine) film.

1. Introduction

The investigation of polymer films on electrode surfaces is one of the most active research areas in the field of contemporary electrochemistry. Electrochemically initiated polymerization has recently received great attention in the modification of electrode surfaces, because of the potential applications (electrocatalysis [1, 2], protection of metals from corrosion (antiphotocorrosion) [3, 4], electrochromic display [5, 6] etc) of the resulting modified electrodes. This procedure also holds great promise for the synthesis of new organic conducting, semiconducting or monoconducting polymers.

The properties and structures of the prepared films depend on the kind of monomer used for polymerization as well as the experimental conditions used in their preparation as substrates, the solvent and the nature of the electrolyte species. By appropriate choice of a monomer and the experimental conditions for preparation, polymer films with a particular desired property can be prepared.

Polyaniline can be electrochemically deposited to give conductive thin films on electrodes [7, 8], and this coating has been applied to silicon in an attempt to stabilize the electrode in aqueous solution [4]. These polymer films prepared by electrochemical polymerization of aniline are conducting or insulating in the dry state and electroinactive in the wet state depending on the experimental conditions used for their electrochemical preparation [2, 7, 9].

In the present paper, we report the preparation of poly(m-toluidine), p-m-tD, films by cyclic voltammetry and potentiostatically and their electrochemical properties and structure. m-Toluidine is a methyl substituent of aniline. The stability of the p-m-tD films as an anion exchanger has been studied.

2. Experimental details

The electropolymerization of m-toluidine was realized by cyclic voltammetry and potentiostatically, using 1 M H_2SO_4 solution containing 0.5 and 0.1 M m-toluidine. The m-toluidine was purified by distillation using standard techniques. The electrolyte was prepared with distilled water and reagent grade sulphuric acid. Gold and tin oxide were used as working electrodes.

Electrochemical potentials were recorded versus a saturated calomel electrode (SCE). The solution was degassed by bubbling nitrogen for at least 15 min before use and nitrogen was passed over the solutions during the experiments. All experiments were performed at room temperature in a three-electrode cell.

Cyclic voltammograms and *I–t* curves were recorded with a Fabell potentiostat (model MA 110-102), and an *X–Y* recorder (Hewlet Packard model 7047 A). The microstructure was determined by scanning electron microscopy.

3. Results and discussion

The cyclic voltammograms recorded during the electropolymerization of p-m-tD on a gold electrode are shown in Fig. 1. At the first cycle, a distinctive wave corresponding to the oxidation of m-toluidine is observed at about 0.70 V/SCE. In the following sweeps, the current in that region decreases rapidly and new oxidation peaks appear in the more negative potential region; this is an indication that m-toluidine oxidizes more readily on the p-m-tD film than on gold. These peaks (0.3 and 0.5 V/SCE) are ascribable to the electrochemical response of the p-m-tD deposit formed during the oxidation process. The corresponding cathodic peaks (0.2 and 0.4 V/SCE) are due to the reduction of the previously generated oxidized species. Repetitive cycling of the potential produces a progressive increase in the voltammetric peaks to an apparent redox system, indicating the build-up of the surface-bound electroactive material [10]. The electrode is covered with a uniform, insoluble and adherent deposit. Coloured, soluble, oligomeric products are seen near the electrode during the electrodeposition process of p-m-tD, which indicates a quantitative polymerization less than 100% yield.

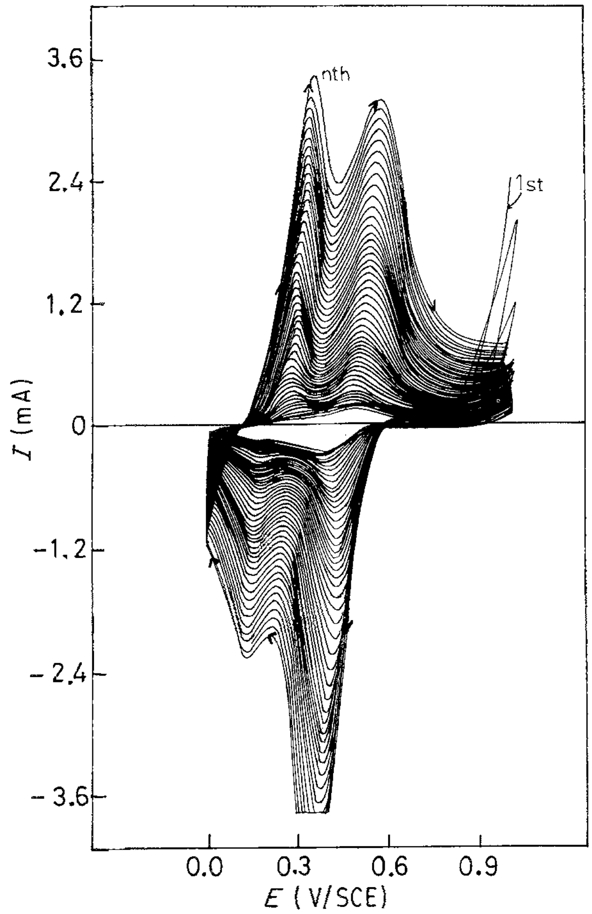

Fig. 1. Cyclic voltammograms of 0.5 M m-toluidine at a gold electrode in 1 M H_2SO_4. Scan rate, 50 mV s^{-1}.

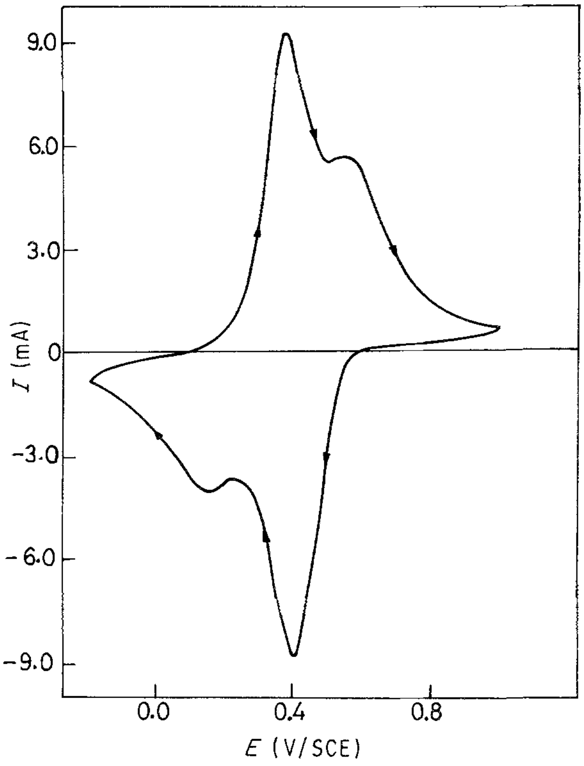

Fig. 2. Voltammogram of poly(m-toluidine) in 1 M H_2SO_4. Sweep rate, 50 mV s^{-1}.

After about 100 cycles between 0.0 and 0.1 V/SCE, p-m-tD was obtained on the gold electrode. When the polymer was very thick the colour was green but during the deposition it exhibited multiple and reversible colour changes from yellow, to blue-violet to green.

The test electrode that had been subjected to prolonged potential cycling in 0.1 M m-toluidine and 1 M H_2SO_4 was again transferred to 1 M H_2SO_4 solution. The cyclic voltammogram in blank solution (Fig. 2) shows two main reversible redox systems (0.38 and 0.55 V/SCE). The redox cycle is quite stable to cycling if the switching potential is kept below 1.3 V/SCE. When the anodic potential reaches values higher than 1.3 V/SCE, as no further processes are observed, the electrode undergoes slow decomposition. The destruction of the polymer can be attributed to irreversible deterioration of the film by formation of electroinactive polymer films on the electrode surfaces. Fig. 3a shows the cyclic voltammogram of p-m-tD film using six different sweep rates in 1 M H_2SO_4 solution containing no monomeric m-toluidine. Fig. 3b indicates that the peak values of the current are linearly related to the square root of the sweep rate; this suggests diffusional control of the rate of the redox reaction.

Several sets of potential step experiments were carried out; the potential was stepped from 0.0 V to values in the range 0.6 V to 1 V/SCE using solutions of 0.5 M m-toluidine and 1 M H_2SO_4. Fig. 4 shows data from two such sets of experiments in the form of I–t transients. At each potential, the charging current by a rising transient is attributable to a nucleation and growth mechanism. Such mechanisms are common for the deposition of conducting phases on another electrode material. The transients peak and the current decreases with time. This behaviour has been observed in the electropolymerization of other polymers; for example, when polypyrrole or poly-N-methylpyrrole are deposited, instantaneous nucleation with three-dimensional growth occurs [11, 12]. The electropolymerization of m-toluidine is similar except that the nucleation process is not instantaneous. The growth on the nucleus needs approximately 6 min at all potentials studied. When the growth begins, the current in the I–t curve also increases producing an increase in the thickness of the polymer. Above the upper limit, the current tends to decay due to diffusion control; at the lower limit slow nucleation causes a continuously increasing current. The form of the I–t transients clearly implicates a nucleation and phase growth process in the mechanism of deposition of p-m-tD films.

At potential values of 0.6 and 0.8 V/SCE a non-homogeneous and poorly adhering deposit was obtained on the electrode after polymerization. At 1 V/SCE a thick dark green film was obtained. The micrograph corresponding to the film at this potential is shown in Fig. 5a. The p-m-tD film obtained had a compact deposit of high porosity which is expected to be easily accessible to the electrolyte.

The microstructure of p-m-tD films prepared by the

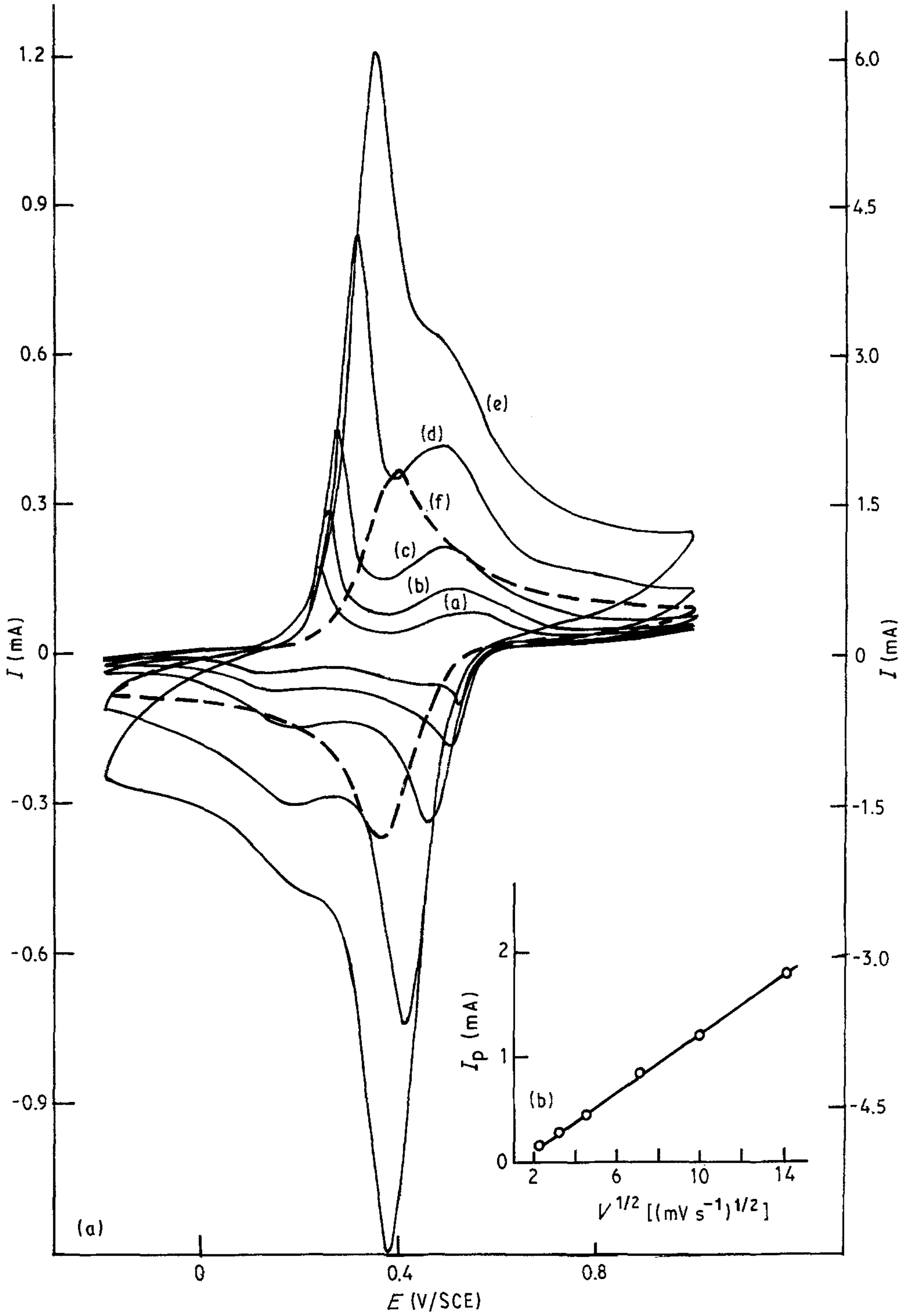

Fig. 3. (a) Cyclic voltammograms showing the electroactivity of polyaniline film on a gold substrate at different scan rates: (a) 5 mV s^{-1} (b) 10 mV s^{-1} (c) 20 mV s^{-1} (d) 50 mV s^{-1} (e) 100 mV s^{-1} (f) 200 mV s^{-1}. Measurements were made in 1 M H_2SO_4 free from m-toluidine. (——) use left-hand scale (— —) use right-hand scale. (b) Study of the first oxidation peak current intensity as a function of scan rate.

sweeping technique and potentiostatically did not have identical characteristics. Figs 5b and 5c show the SEMS of p-m-tD films obtained by cyclic voltammetry. This film has a granular structure in the form of balls on previously formed nuclei. Fig. 5c is the same film at high magnification and the above mentioned growth can be more clearly observed. When the p-m-tD film was obtained on tin oxide with the same technique it had a compact structure on which soft fibres were superimposed. The fibrous structure was visible to the naked eye and was confirmed by SEM (Fig. 5d).

Elemental analysis of a polymer sample obtained by cyclic voltammetry was carried out. A composition 55 · 16% C, 5 · 0% H, 8 · 47% N and 31 · 37% (S+O) was found. The C/N ratio was 6.5 for the polymer and 7 for the monomer.

The oxidation and reduction of redox species in aqueous solutions were driven in the potential range between 0.12 and 1.1 V/SCE. Fig. 6 shows cyclic voltammograms at different sweep rates, of the redox reaction Fe^{2+}/Fe^{3+} in 1 M H_2SO_4. The Fe^{2+}/Fe^{3+} redox peaks appear superimposed on the background electroactivity of the film and occur around +0.44 V which is the equilibrium potential of Fe^{2+}/Fe^{3+}

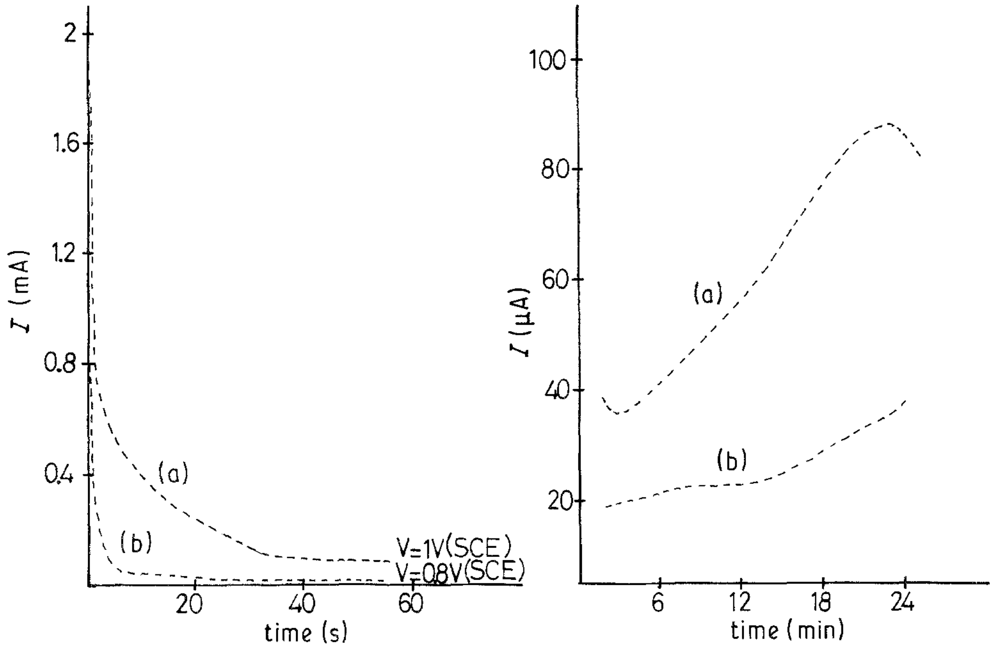

Fig. 4. I–t transients in response to potential steps from (a) 0.0 to 1 V and (b) 0.0 to 0.8 V. 0.5 M m-toluidine solution in 1 M H_2SO_4, gold electrode.

measured in the same solution with a gold electrode. The reaction on Au/p-m-tD is that of a surface-bound species, as evidenced by the shape of the waves, however, the peaks do not coincide, nor do their heights vary linearly or as the square root with scan rate. This suggests a diffusional contribution by the species through the film. The current increases with increase in the bulk concentration of Fe^{2+}. The separation between the anodic and cathodic peak potentials, ΔE_p, varies with v. The value of ΔE_p exceeds the

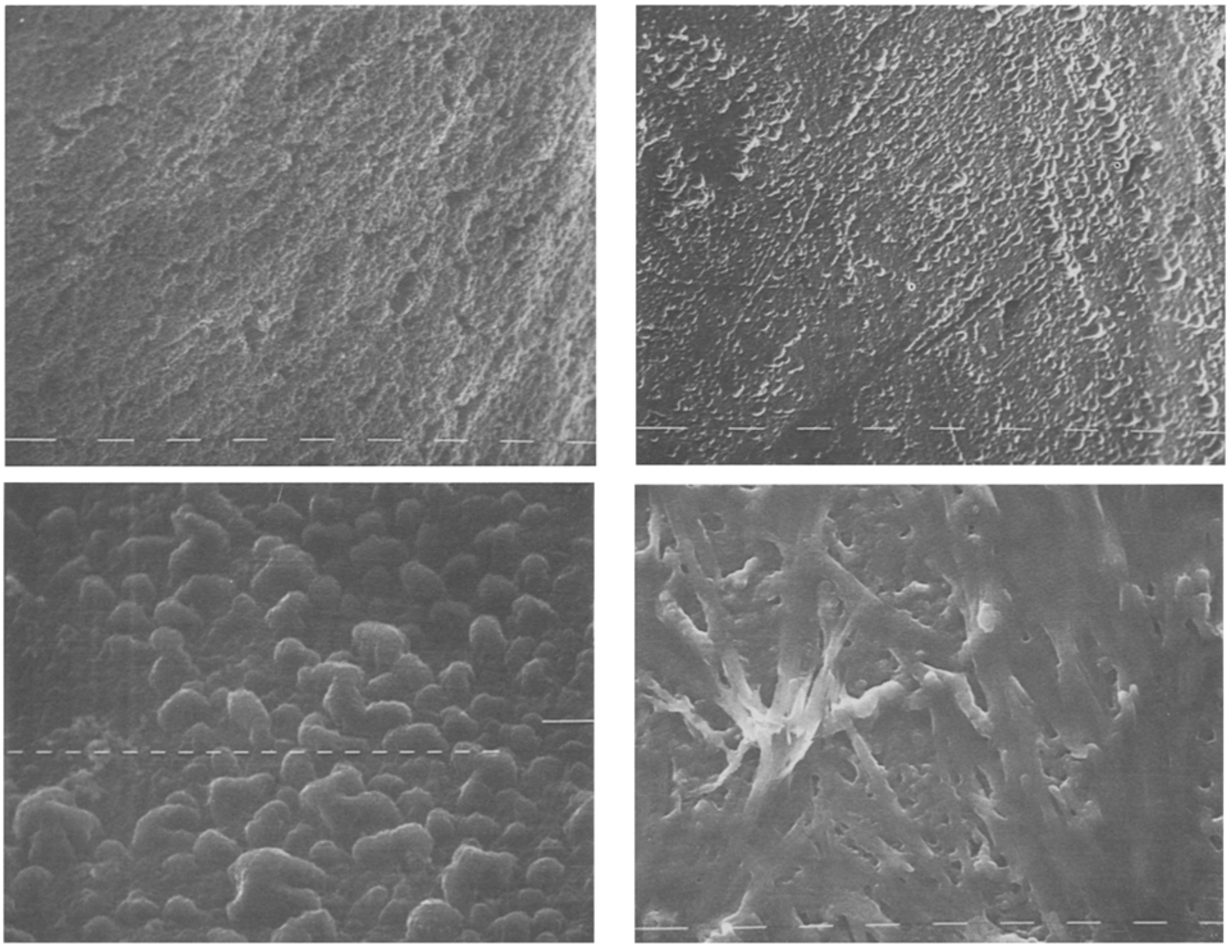

Fig. 5. Electron micrographs of films, grown in 1 M H_2SO_4 + 0.5 M m-toluidine: (a) at 1 V vs SCE during 30 min on a gold electrode (×640) (b) by cyclic voltammetry ≃ 100 cycles on a gold electrode (×640) (c) the same film as (b) magnified ×2500 (d) by cyclic voltammetry ≃ 100 cycles on tin oxide (×640).

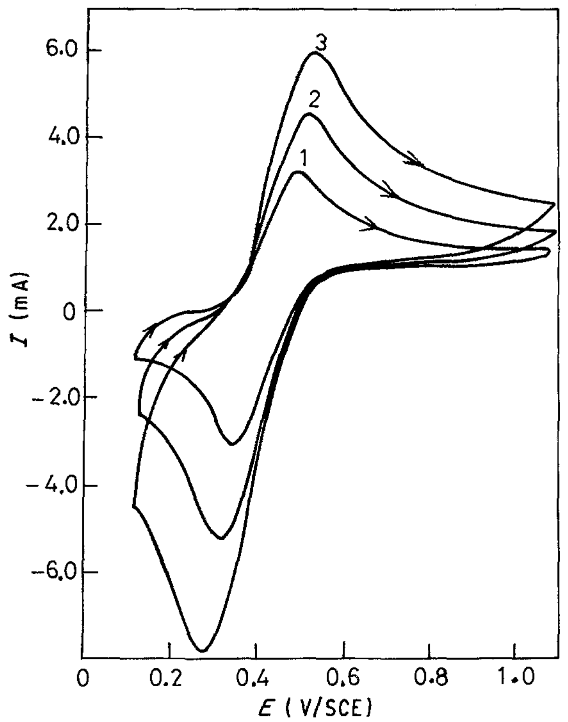

Fig. 6. Cyclic voltammograms of a film of p-m-tD in contact with 10^{-1} M $FeSO_4$ solution at sweep rates of (1) $20\,mV\,s^{-1}$ (2) $50\,mV\,s^{-1}$ and (3) $100\,mV\,s^{-1}$.

expected value 0.059 V diffusion-controlled, reversible waves. This is attributed to slow, heterogeneous electron transfer between the electrode and the redox centres in the film and uncompensated film resistance, which is the resistance to ion flow through the film caused by low ambient ion populations and/or sluggish ion mobility.

4. Conclusions

Potentiodynamic electropolymerization of m-tD in 1 M H_2SO_4 leads to the formation of uniform and adherent films of p-m-tD.

The m-toluidine polymer is much more resistant than polyaniline to exposure to high positive potentials; this is one of the disadvantages of polyaniline [13].

The investigated m-toluidine polymerized in an acid medium tail-to-tail and head-to-tail respectively. The polymer is electroactive in acid medium, in which it is oxidized in two steps.

The substrate determines the structure of the polymer; on a gold electrode the structure is globular and on tin oxide it is fibrous.

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