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KINETICS AND MECHANISM OF ELECTRO-OXIDATIVE POLYMERIZATION OF *m*-CRESOL ON Pt ELECTRODE CATALYSED BY TRIMETHYLAMINE

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Abstract—The kinetics and mechanism of electropolymerization of *m*-cresol (mC) on Pt electrode catalysed by trimethylamine (TMA) has been studied in acetonitrile. The rate of polymerization shows first order dependences on monomer concentration and current and fractional order on [TMA] at lower current densities; at higher current densities, the rate is independent of current density. A suitable mechanism has been proposed and a rate equation is derived to explain the observed features. Rotating disc studies reveal that, at low current densities, the rate of polymerization is charge-controlled but, at high current densities, it is diffusion-controlled. Conditions for obtaining selective products with high current efficiency have been established. Factors limiting film thickness have been identified.

INTRODUCTION

The study of electropolymerization is still in its infancy. Although, the viability of electropolymers has been amply demonstrated, it is clear that there are still problems of development [1]. By studying the kinetics of electropolymerization, important activation and thermodynamic quantities can be determined; such studies are however very scarce [2]. Fundamental models of industrial scale polymerization are lacking largely because of the absence of a partial-current electrode kinetic model [3]. In order to develop new devices based on polymer coated electrodes, it is necessary to clarify the charge transport processes [4].

Several phenols have been electropolymerized mainly for corrosion protection [5] because the polymers are chemically inert undergoing almost no oxidation or hydrolysis in either basic or acidic media. Moreover they are hard and thermally stable. These properties coupled with wear resistance and fine gloss make polyoxyphenylenes ideal candidates for providing a cheap and simple way of protecting metals. Further, phenols are electropolymerized for deposition of reactive [6] and conductive [7] films and production of potentiometric sensors [7].

A suitable coating must be adherent, scratch resistant, flexible and resistant to aqueous acids and alkalis and to common solvents. Further, most importantly, the rate and efficiency of conversion of the monomer to polymer must approach the high values already available using conventional roller coating techniques for applying prepared lacquers. Surprisingly little information has been published in this connection.

We have found that *m*-cresol (mC) electropolymerized in the presence of trimethylamine (TMA) has remarkable properties of corrosion protection and thermal stability. The same polymer is formed on both Pt [8] and Fe [9] electrodes. In this paper, an investigation of the kinetics and mechanism of the electropolymerization of mC catalysed by TMA is presented to discover whether the rates of coating are sufficient to replace conventional techniques like lacquering. Although the same coating was obtained on Pt and Fe, the kinetic study was made only with Pt because the anodic dissolution kinetics of Fe are likely to interfere and to complicate the kinetics of polymerization.

EXPERIMENTAL PROCEDURES

All reagents were of Analar grade. The monomer, $NaClO_4$ acetonitrile (AN), conductivity water and TMA were purified by standard procedures. Polymerization was carried out under N_2 in a H-shaped cell divided into two compartments by a glass sintered disc. Pt foils of 1 and 5 cm^2 were used as anode and cathode, respectively (change in the size and shape of the anode has little effect). The cell assembly was thermostated at 298 ± 1 K and reaction mixtures containing the required amounts of monomer and TMA in AN as solvent were degassed by passing N_2. Electrolysis was carried out using a homemade constant power d.c source with an accuracy of 0.10 μA. Polymer yield was obtained gravimetrically from the difference in weights of Pt samples (anode; no change occurs in the cathodic compartment) before and after the experiment. The experiments were repeated (5–7 times) and the mean yields are presented with an accuracy of $\sim$1–5 μg. The intrinsic viscosity measurements were made in DMSO. RDE experiments were conducted on a Taccusel Pt RDE.

RESULTS AND DISCUSSIONS

No polymerization was observed in the absence of current, ruling out thermal polymerization; in the absence of TMA, no coating was observed but the electrolyte turned brown with intensity increasing with time (Fig. 1). The anode was coated with brown film within a few seconds, when current was passed through the AN solution containing 0.1 M mC and 0.1 M TMA. The film formed was insoluble in the medium and the thickness of the film increased with

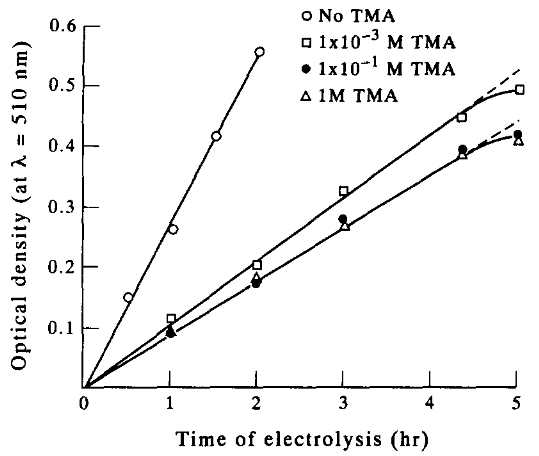


Fig. 1. Intensity of the electrolyte vs time of electrolysis for solution; AN + 1 × 10^{-1} M $NaClO_4$ 1 × 10^{-1} M mC at 0.1 mA/cm^2.

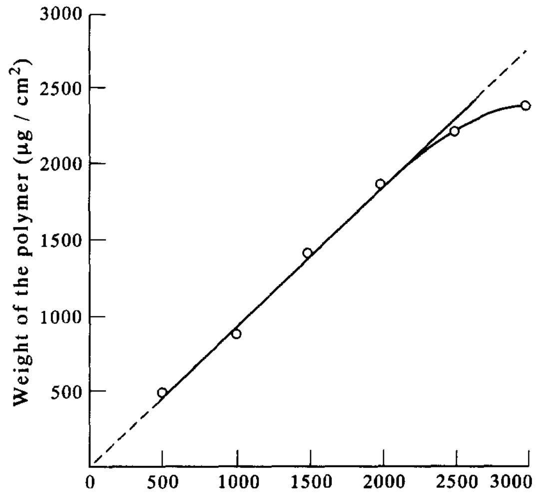


Fig. 2. Dependence of weight of polymer on time of electrolysis. [mC] = 1 × 10^{-1} M; [TMA] = 1 × 10^{-1} M; current = 0.1 mA/cm^2, solvent = AN.

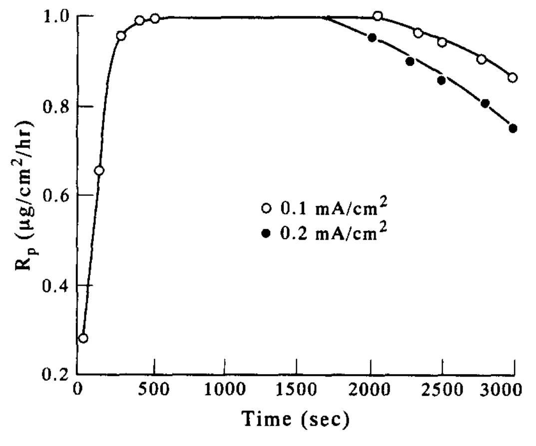


Fig. 3. Dependence of R_p on the time for electropolymerization of mC in AN; [mC] = [TMA] = [$NaClO_4$] = 1 × 10^{-1} M.

Table 1. Variation of R_p with [$NaClO_4$] for the electropolymerization of mC in AN containing 0.1 M mC and 0.1 M TMA at 0.1 mA/cm^2

Concentration of $NaClO_4$(M)	R_p(μg/cm^2/sec)
1 × 10^{-2}	0.2784
5 × 10^{-2}	0.6800
1 × 10^{-1}	1.0058
1.5 × 10^{-1}	1.0050
2 × 10^{-1}	1.0056
1	1.0049

time. Simultaneously, the solution in the vicinity of the anode also became coloured and the intensity increased with time (Fig. 1). The intensity and its increase are less when TMA is present. Figure 2 gives the (weight of the polymer coated)–time curves; steady states were obtained in about 300 sec and remained up to ~2000 sec, beyond which it appeared to be saturated. The rate of polymerization (R_p) was calculated as the weight difference of the electrode before and after electrolysis and is reported as μg/cm^2/sec. R_p remained constant within experimental error for a given condition, irrespective of the size and shape of the electrodes indicating uniform current distribution. R_p was independent of time between 30 and 2000 sec, but later it decreased (Fig. 3).

R_p was low at low [$NaClO_4$] and increased with [$NaClO_4$] reaching a maximum at ~0.1 M $NaClO_4$ beyond which it was independent of [$NaClO_4$] (Table 1). R_p showed $[mC]^1$ $[TMA]^{0.75}$ (current) order dependency in the range 0.02–0.1 mA/cm^2 current density, beyond which it was independent of current density (Fig. 4).

The intrinsic viscosities of the polymers in DMSO are given in Table 2; the quantity constant for polymers prepared under particular conditions.

In the light of these results and earlier literature on anodic oxidation of phenols [10–14], making the reasonable assumption that the effect of $NaClO_4$ was only to improve the conductivity of the solution, Scheme 1 may be proposed for the anodic oxidative polymerization of mC.

pKa (10.00) values of mC indicates that the equilibrium between molecular mC(I) and the 3-methylphenoxide ion [15, 16] (II) lies towards molecular mC; the undissociated mC undergoes a two-electron anodic oxidation with simultaneous removal of hydrogen ion forming the phenoxonium ion (III) [17]. The phenoxonium ions are reactive electrophiles and hence there is a coupling reaction involving electrophilic attack of an anodically generated phenoxonium ion on the starting mC to form dimer (IV), which is soluble in the medium. On the

Table 2. Intrinsic viscosities of mC polymers in DMSO

Duration of electrolysis* (sec)	Intrinsic viscosity
300	0.22
600	0.24
900	0.23
1200	0.21
1200 (at 10.0 mA/cm^2)	0.22

*In AN containing 0.1 M mC, 0.1 M TMA and 0.1 M $NaClO_4$ at 0.1 mA/cm^2.

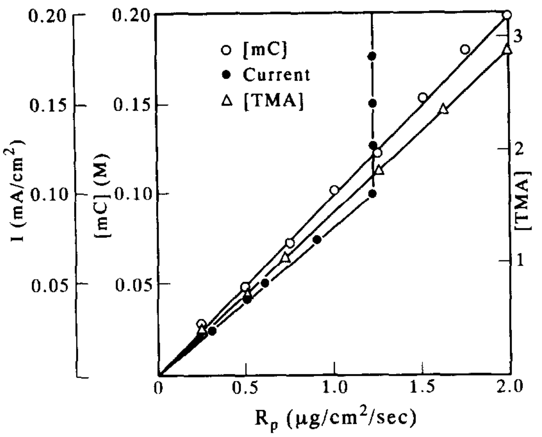


Fig. 4. Dependence of R_p on [mC], (CURRENT) and $[\mathrm{TMA}]^{0.75}$ for the electropolymerization of mC in AN containing 1×10^{-1} M $NaClO_4$ at 303 K.

other hand, 3-methylphenoxide ion (**II**) is produced in the presence of TMA by the abstraction of protons; an anodic oxidation, (**II**) produces the phenoxy radical (**V**) by one-electron removal and C—O coupling between the phenoxy free radicals is expected to occur preferentially since the phenoxy free radical is unreactive in an electrophilic substitution reaction.

Thus if mC is in the undissociated form, C—C coupling occurs primarily and the main product is the soluble dimer; if it is in the dissociated form (brought out by the abstraction of protons by TMA), C—O coupling occurs to form the polymer.

Applying the stationary state approximation to species **II** in Scheme 1.

$$\frac{d(\mathrm{II})}{dt} = k_f[\mathrm{mC}][\mathrm{TMA}] - k_r[\mathrm{II}][\mathrm{TMA}^+] - k_2[\mathrm{II}](\mathrm{current}) = 0$$

neglecting $k_2[\mathrm{II}]$ (current), with the reasonable assumption that **II** remains at its equilibrium level undisturbed by slow formation of **V**.

$$(\mathrm{II}) = \frac{k_f[\mathrm{mC}][\mathrm{TMA}]}{k_r[\mathrm{TMA}^+]} = \frac{K[\mathrm{mC}][\mathrm{TMA}]}{[\mathrm{TMA}^+]} \qquad (1)$$

Where K is the equilibrium constant. Applying the stationary state approximation to [**V**].

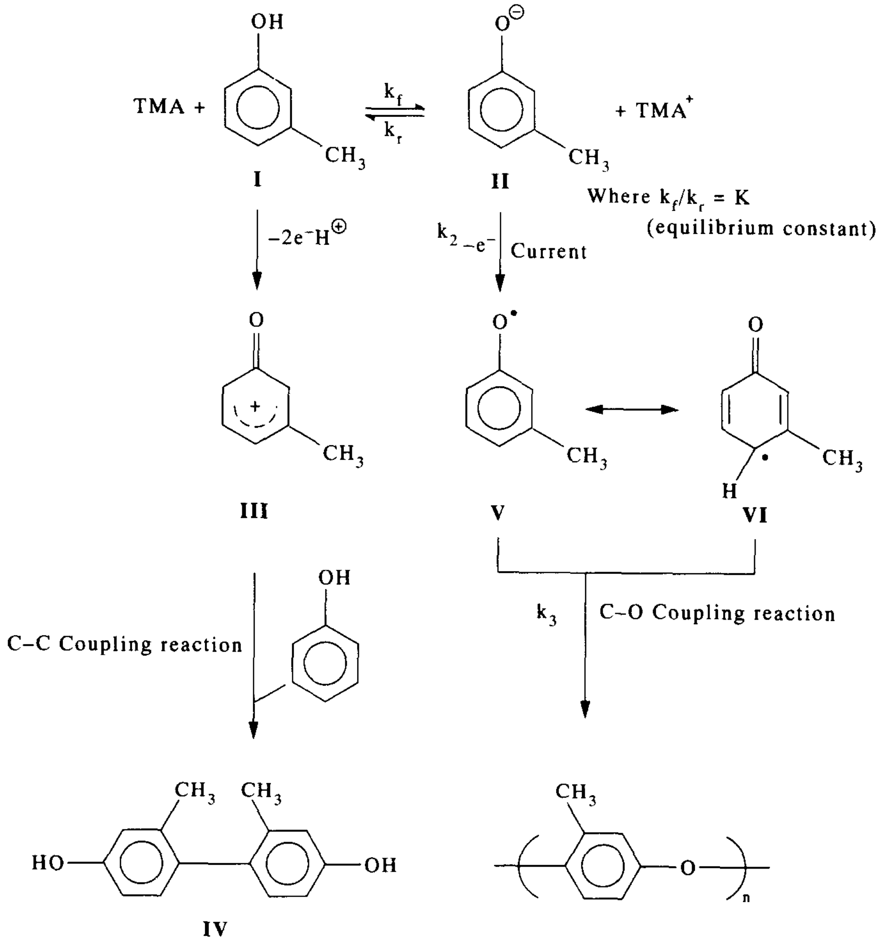
$$\frac{d[\mathrm{V}]}{dt} = k_2[\mathrm{II}](\mathrm{current}) - k_3[\mathrm{V}][\mathrm{mC}] = 0$$

but

$$R_p = k_3[\mathrm{V}][\mathrm{mC}]$$

so that

$$R_p = k_2[\mathrm{II}](\mathrm{current}) \qquad (2)$$



Scheme 1. Mechanism of electropolymerization of *m*-cresol.

from equations (1) and (2),

$$R_p = \frac{K_2K[\text{mC}][\text{TMA}](\text{current})}{[\text{TMA}^+]}.$$

This equation is in agreement with the experimental finding

$$R_p \propto [\text{mC}](\text{current})[\text{TMA}]^{0.75}.$$

The fractional order dependence of R_p on [TMA] deserves comment. In TMA, the presence of three electron-releasing methyl groups increases the electron density of the N atom and hence increases the basicity and the proton abstraction strength. The resulting $(CH_3)_3NH^+$ is sterically hindered because of the crowding of three bulky methyl groups in addition to hydrogen and so it is unstable, resulting in the dissociation of TMA^+. The dissociation of TMA^+ (to TMA + H^+) furnishes more and more H^+ ions which in turn react with 3-methylphenoxide ion to produce mC. Thus there is no possibility of increasing R_p by the presence of excess TMA. This point also explains why, even in the presence of TMA, dimer formation is not prevented (Fig. 1).

The independence of R_p of current at higher current densities (not apparent from the rate equation) may be due to one of the following reasons.

(a) At higher current densities, deterioration of the film may occur because of its oxidation. It has been observed, however, that the polymer was highly stable and electro-inactive [8] and even the passage of 10 mA/cm^2 of current for 600 sec did not produce any change in the properties of the film (Table 2).

(b) The electrode coated with the polymer might behave differently and as a consequence the rate might change. On a polymer modified electrode, the reaction takes place:

(i) on the surface of the polymer film;
(ii) at the polymer/electrolyte interphase;
(iii) at the polymer/electrode interphase; or;
(iv) on the electrode itself by the diffusion of the monomer through the polymer coating.

In order to to understand the effect, one has to consider the diffusion of the monomer through the polymer. However, it was observed that the electrode was coated with polymer almost instantaneously on passage of current and the coating on the electrode, at least up to a certain thickness, had no effect on R_p (Figs 2 and 3). Hence modification of the electrode surface might not be the reason for the observed R_p-current relation at higher current densities.

(c) On the other hand, one could suppose that, at low current density, the rate of charge transfer is low in comparison to that of the diffusion process and hence R_p is charge-controlled at low current densities. As the current density is raised, the charge transfer rate would increase accordingly and, at sufficiently high current density, the charge transfer might become so high that the rate of polymerization might become diffusion-controlled because of the fast depletion of the species in the vicinity of the electrode. As a consequence, R_p would become independent of current at higher current densities.

Any factor that would increase the rate of diffusion would also increase R_p. In order to confirm this point, R_p values were obtained at different rotation speeds at various current densities (Fig. 5). It has been observed that, at low current densities, R_p is independent of rotation speed indicating that the reaction is charge-controlled; at higher current densities, R_p increased with rotation speed indicating that the reaction is diffusion-controlled.

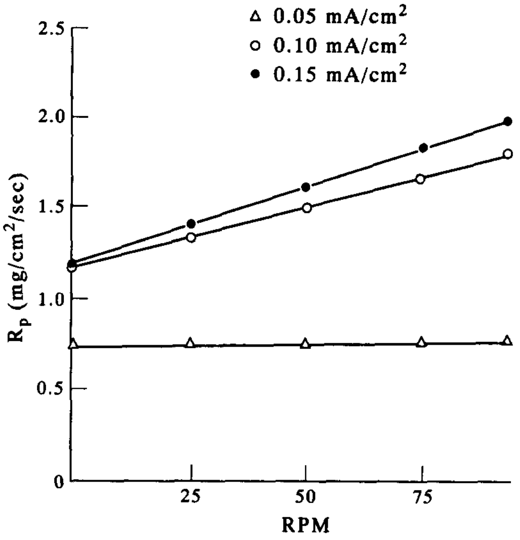


Fig. 5. Dependence of R_p on rotational speed of electrode for the electropolymerization of mC from AN containing mC (0.1 M) + TMA (0.1 M) + $NaClO_4$ (0.1 M).

The R_p–time graph (Fig. 3) shows that R_p remained independent of time for a certain period beyond which it decreased. The range for which R_p was independent of time varied with current density (the higher the current density, the smaller the range). These results indicate that the coating was porous up to a certain thickness and free passage of monomer could occur. Beyond a certain thickness, the coating might become compact so that the diffusion of the monomer is impeded, if the reaction takes place on the electrode surface. On the other hand, if the reaction occurs on the polymer surface, R_p might decrease because of the decrease in charge available as the polymer is a poor conductor [8]. In either case, one would expect a decrease in R_p after prolonged electrolysis. In other words, a coating exceeding a certain thickness cannot be achieved.

Table 3 summarizes the current efficiencies for various oxidation products of mC. It is observed that the current efficiency for dimer formation is remarkedly decreased in the presence of TMA, while that of polymer increases and reaches a maximum. Further increase of current efficiency of polymer formation is not possible mainly because of the interference of

Table 3. Current efficiencies for products from mC

Conditions		Current efficiency	
Conc. of TMA (M)	Current density (mA/cm^2)	Dimer	Polymer
Nil	0.1	52	Nil
1×10^{-2}	0.1	30.4	17.6
5×10^{-2}	0.1	17.8	41.2
1×10^{-1}	0.1	15.6	52.4
5×10^{-1}	0.1	16.0	52.8
1×10^{-1}	0.2	15.8	51.4

the TMA^+ dissociation equilibrium with the mC dissocation equilibrium as discussed earlier.

CONCLUSIONS

The results indicate that electropolymerization of mC occurs in the presence of TMA catalyst at sufficiently high rate on Pt. Uniform polymer coatings can be obtained with a current efficiency of about 60%. Further increase of current efficiency is not possible as a consequence of the dissociation of protonated TMA. The thickness of the coating cannot be increased beyond a certain value because of resistance of the film and/or because of sealing of the pores in the film. The self limiting phenomenon with respect to thickness ensures uniform current distribution and hence electrodes of various size and shapes can be easily coated with non-porous, stable (to chemicals and heat) and uniform poly (mC).

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