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Electropolymerization of *m*-cresol in the presence of trimethylamine

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The feasibility of anodic electropolymerization of *meta* cresol (*m*C) in the presence of trimethylamine (TMA) was demonstrated on a platinum electrode in acetonitrile (AN), tetrahydrofuran (THF), *n*, *n*-dimethyl formamide (DMF) and methanol (MeOH) solutions. In DMF and MeOH, due to the adsorption of TMA on the electrode, the electropolymerization occurs in the vicinity of the electrode rather than on the electrode surface. The coatings obtained have poor corrosion inhibition characteristics. But in AN and THF, thin coatings were obtained on the electrode as *m*C is preferentially adsorbed rather than TMA and, subsequently, the electropolymerization takes place on the electrode surface. The polymers obtained have remarkable corrosion protection and thermal stability. The polymers contain C–O–C linkages and have no troublesome nitrogen content.

1. Introduction

Polyoxyphenylenes exhibit some unique properties which make them very attractive candidates for use as materials for protective coatings. They are chemically inert compounds undergoing almost no oxidation or hydrolysis in either basic or acidic media. Moreover, they are hard and thermally stable. Because of their hardness and wear resistance, electrochemically produced polyoxyphenylenes may provide a cheap and simple way of protecting metals [1]. But, in spite of these important advantages, progress towards optimization of polyoxyphenylene coatings is greatly hindered primarily due to the lack of stable coatings [2]. The main reason for this situation is the fact that most of the phenols are polymerized only in the presence of aliphatic amines. These amines, besides playing an important role during the electropolymerization of phenols (by entering into competitive adsorption on the metal surface [3–8] or by abstraction of the protons [9] during electropolymerization) are substantially present in the polyoxyphenylenes. Pyrolysis mass spectrometry reveals that amine was directly bound to polyoxyphenylene chains and not just entrapped in the polymer network [10]. The numerous amino groups may represent hydrophilic oxidizable easily attackable moieties, thus compromising chemical stability and, consequently, the protective capacity of the coatings. Thus, even though amines are required for electropolymerization of phenols, their adsorption during electropolymerization and, as a consequence, their presence in the polymer, should be avoided.

To achieve this goal, a system has been chosen in which a phenol having greater tendency to adsorb (*m*-cresol) has been electropolymerized in the presence of an amine having lesser tendency to adsorb. In *m*-cresol (*m*C) the presence of *m*-methyl group reinforces the electron density of oxygen and hence the adsorption. In trimethyl amine the presence of three bulky methyl groups prevent effective adsorption (due to steric hindrance) while increasing the proton acceptor character. Using this system it is possible to obtain poly *m*C which has no nitrogen content and has good corrosion protective characteristics and remarkable thermal stability.

2. Experimental details

The experimental set up included a Taccussel (PRT-10-0.5) potentiostat commanded by a Taccussel (GSTP-3) signal generator and the cyclic voltammograms were recorded on a Sefram recorder (*XYt*). A three-compartment cell was used with platinum ($1 \times 1\,cm^2$), platinum ($5 \times 5\,cm^2$) and saturated calomel electrode (SCE) as working, counter and reference electrodes respectively. AR grade *m*C, solvents and $NaClO_4$ were used. The electrodes were purified by usual procedures. The experiments were conducted at 303 ± 1 K.

For constant potential electrolysis a Taccussel (PRT-10-0.5) potentiostat was used with a two-electrode system.

The perchlorate ion content of the polymer was determined by suspending the polymer sample in a small amount of concentrated H_2SO_4. The $HClO_4$ was distilled and was absorbed in dilute NaOH solution. The resulting solution was subjected to colorimetry with methylene blue [11,12].

For the corrosion inhibition study, a calculated amount of the coating was dissolved in DMSO and sprayed on copper sheets ($5 \times 5\,cm^2$) and dried at 100 °C. The dried samples were exposed to aerated 1 M H_2SO_4 solution for definite intervals of time. The amount of copper dissolved was estimated colorimetrically using sodium diethyldithiocarbamate. The detailed procedure has been discussed elsewhere [13].

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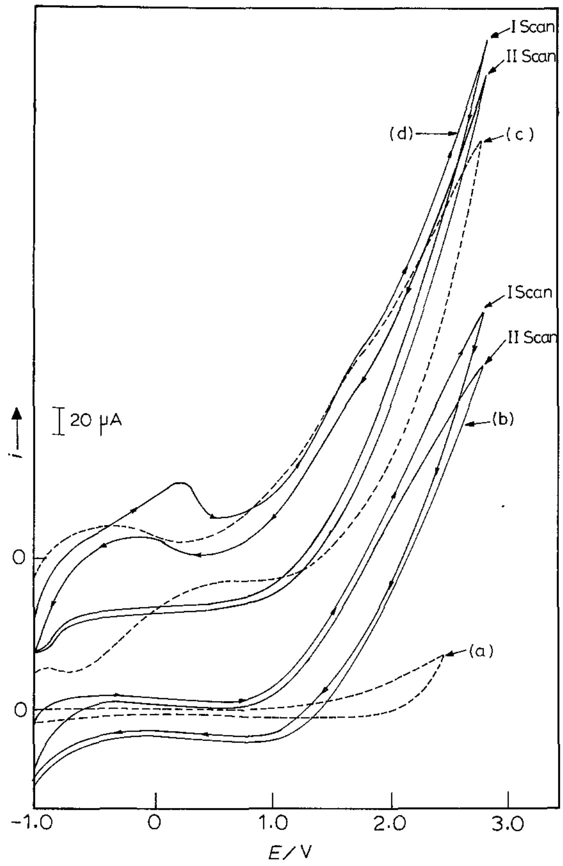


Fig. 1. CVs at Pt in: (a) 0.1 M $NaClO_4$-DMF (----); (b) (a) + 0.05 M *m*C (——); (c) (a) + 0.02% Me_3N (----); (d) (a) 0.05 M *m*C + 0.02% Me_3N (——). Scan rate: 100 mV s^{-1}.

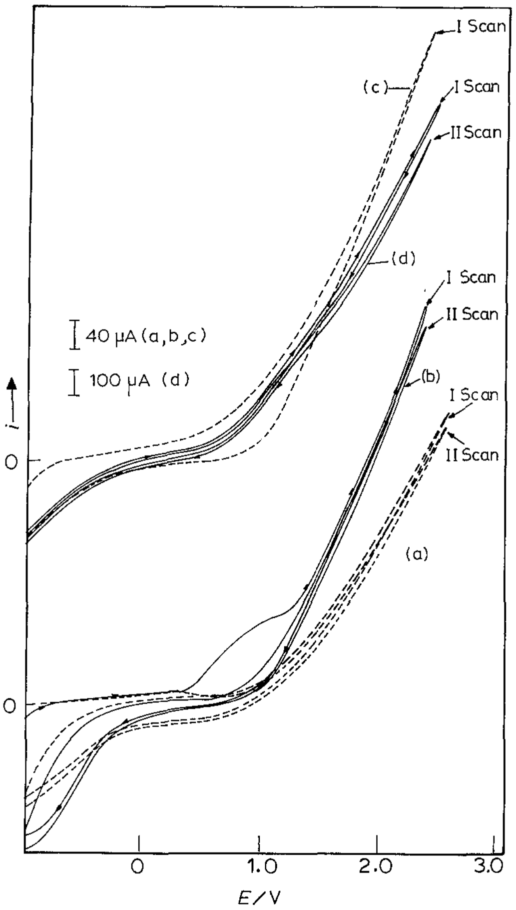


Fig. 2. CVs at Pt in: (a) 0.1 M $NaClO_4$-CH_3OH (----); (b) (a) + 0.05 M *m*C (——); (c) (a) + 0.02% Me_3N (----); (d) (a) + 0.02% Me_3N + 0.05 M *m*C (——). Scan rate: 100 mV s^{-1}.

3. Results and discussions

3.1. *Cyclic voltammetry*

Figure 1a represents the cyclic voltammetry CV run in DMF containing 0.1 M $NaClO_4$. The oxidation of the solvent occurs at + 2.4 V and its reduction at − 1.0 V during the reverse cycle. Addition of TMA gives rise to an additional anodic peak at − 0.3 V and a cathodic peak at − 0.7 V with an increase in anodic current at + 2.4 V (Fig. 1b).

Addition of *m*C to DMF produced no change in its CV except for an increase in the anodic current at + 2.4 V (Fig. 1c). Repeated cycling, even though it enhanced the brown colour intensity in the anodic chamber, produced no coating whatsoever on the surface. The simultaneous presence of *m*C and TMA in DMF produced a shift in the anodic peak corresponding to TMA adsorption in the positive direction and further enhanced the anodic peak current at + 2.4 V (Fig. 1d). Repeated cycling resulted in a yellow coating on the anode. Similar results were observed in MeOH except for some slight variation in peak currents and peak potentials (Fig. 2). In AN and THF, although the results were essentially the same, the anodic peak due to TMA was found to be missing (Figs 3 and 4).

3.2. *Potentiostatic experiments*

The electropolymerization of *m*-cresol was carried out in AN, MeOH, THF and DMF containing 0.1 M $NaClO_4$ at + 2.4 V in the presence and absence of TMA. 2 ml aliquots of the anolyte were withdrawn after a certain amount of charge had been passed and the variation in the colour intensity was analysed spectrophotometrically at a wavelength of 510 nm. The variation of colour intensity of the anolyte with amount of charge (Q) (Fig. 5), concentration of TMA (Fig. 6) and with solvents (Figs 5 and 6), reveal that the intensity increased with charge (Q), and decreased with TMA concentration and with solvents in the order AN < THF < MeOH < DMF, respectively. The electrode was simultaneously coated with a yellow film depending on the concentration of TMA. The weight of the film material, as determined from the difference in weight of the working electrode before and after electrolysis, and thickness (d = weight/electrode surface area × density of the film) [2] are given in Table 1.

3.3. *I.r. analysis*

Comparison of i.r. spectra of *m*C, poly(*m*C)$_{AN}$ and poly(*m*C)$_{DMF}$ (Fig. 7a, b and c) revealed common absorption bands at (i) 2920 cm^{-1} (C=C stretching), (ii) 2854 cm^{-1} (C–H stretching), (iii) ~ 741 cm^{-1} (C–H out of plane bending), (iv) 690 cm^{-1} (C–C out of plane bending), and (v) 1659 cm^{-1} (skeletal in plane vibration of aromatic structure) all characteristic of

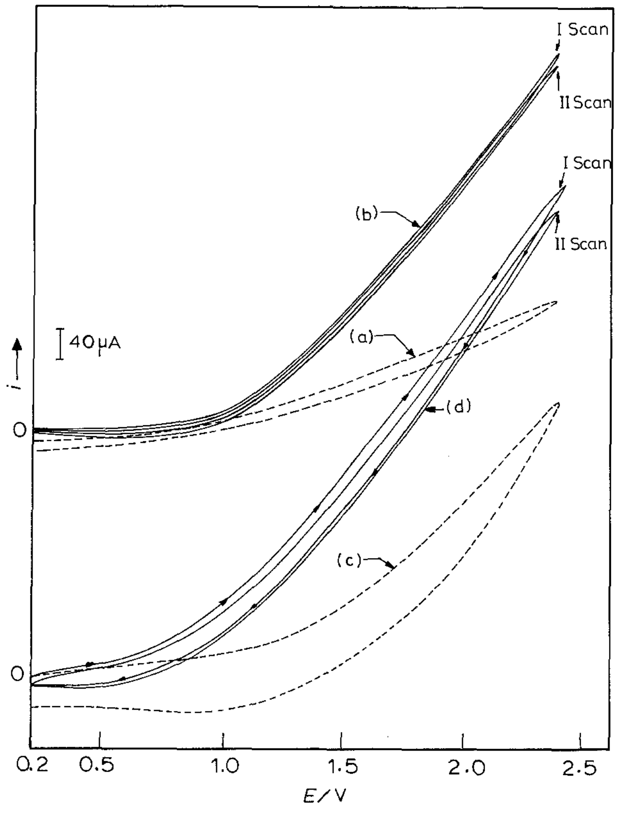


Fig. 3. CVs at Pt in: (a) 0.1 M $NaClO_4$-AN (----); (b) (a) +0.05 M *m*C (——); (c) (a) +0.02% Me_3N (----); (d) (a) +0.02% Me_3N + 0.05 M *m*C (——). Scan rate: 100 mV s^{-1}.

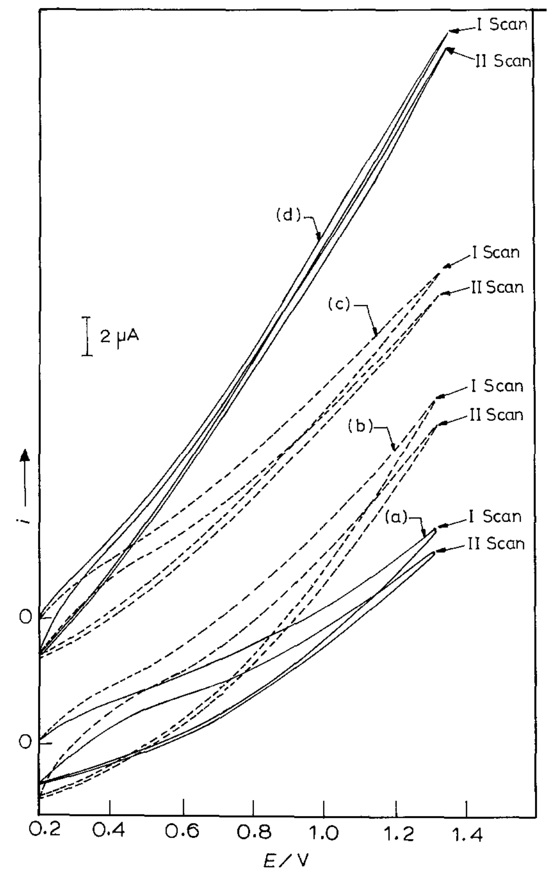


Fig. 4. CVs at Pt in: (a) 0.1 M $NaClO_4$-THF (----); (b) (a) +0.01 M *m*C (----); (c) (a) +0.02% Me_3N (----); (d) (a) +0.02% Me_3N + 0.01 M *m*C (——). Scan rate: 100 mV s^{-1}.

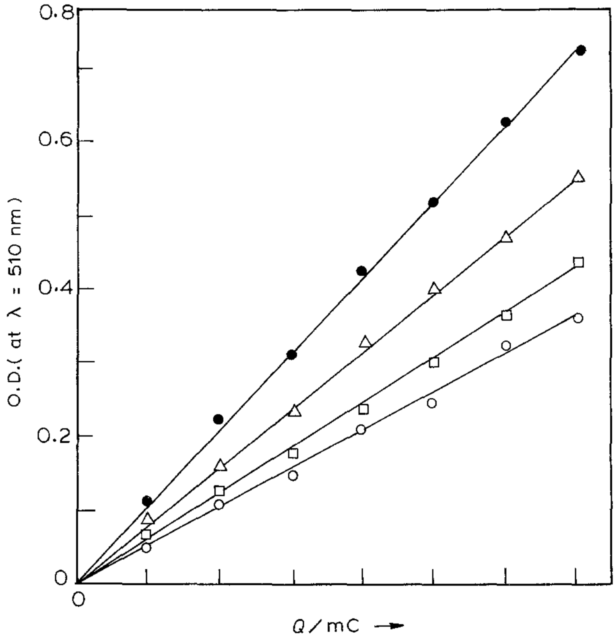


Fig. 5. Dependence of intensity with amount of charge passed during electropolymerization of *m*-cresol. (○) AN, 45 mC cm^{-1}; (□) THF, 60 mC cm^{-1}; (△) MeOH, 90 mC cm^{-1}; and (●) DMF, 100 mC cm^{-1}.

aromatic compounds. The disappearance of the absorption band at 3304 cm^{-1} (O–H stretch found in *m*C) in the i.r. spectra of poly(*m*C)$_{AN}$ and poly(*m*C)$_{DMF}$ and appearance of peaks at ~1215 cm^{-1} indicate the absence of free O–H groups and the presence of C–O–C linkages in the polymer. Again the appearance of additional bands at 816, 981 and 1104 cm^{-1}, characteristic of 1,3,4 substitution, favours the following

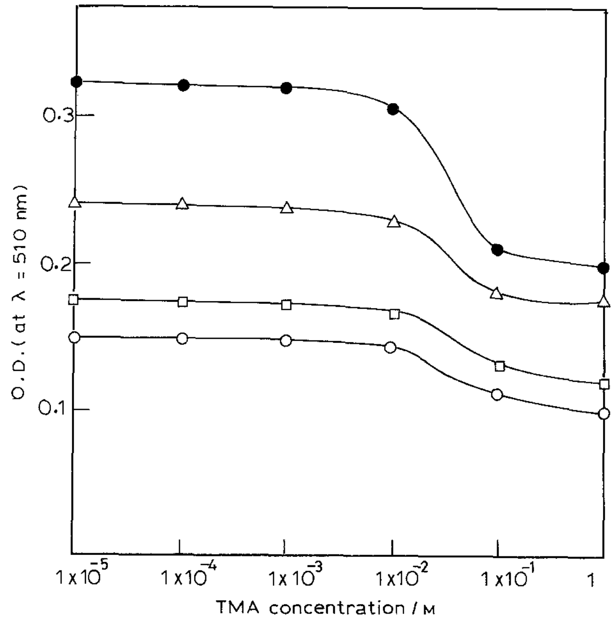


Fig. 6. Dependence of intensity of anolyte with TMA concentration during electropolymerization of *m*-cresol at 2.4 V and for the passage of (●) 720 mC (DMF), (△) 720 mC (MeOH), (□) 490 mC (THF) and (○) 350 mC (AN).

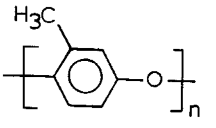
Table 1. Weight of poly(mC) coated on platinum

Solvents	*TMA Concn.* /M	*Polymer weight** /$\mu g\,h^{-1}$	*Thickness*† /μm
AN	-	0.0^a	-
AN	0.01	3.6	1.81
AN	0.1	4.4	2.22
AN	1.0	4.7	2.37
THF	-	0.01^b	0.005
THF	0.01	3.9	1.96
THF	0.1	8.8	4.44
THF	1.0	9.4	4.74
MeOH	-	0.4^c	0.20
MeOH	0.01	6.4	3.23
MeOH	0.1	25.6	12.92
MeOH	1.0	27.2	13.73
DMF	-	0.4^d	0.20
DMF	0.01	8.4	4.24
DMF	0.1	34.6	17.47
DMF	1.0	37.8	19.09

* Corresponding to a passage of (a) 350, (b) 490, (c) 720 and (d) 730 mC.

† Density of the film material: 1.98 g cm^{-3}.

polymer structure:



3.4. *Mechanism of electropolymerization*

An overview of the electropolymerization conditions of various phenols is presented in Table 2. The electron density on the 'O' atom of the OH group increases in the order PhOH < *m*-cresol < 2,6 dimethylphenol [14].

Table 2. An overview of conditions for electropolymerization of phenols

Monomer	*pK$_a$ of monomer*	*Solvents*	E_{pa} /V	*Electrode*	*Ref.*
Phenol	9.99	Oxalic acid	1.0	Pt	2
Phenol	9.99	AN	1.5	BPG	21
2,6-dimePhOH	10.59	AN	1.6	BPG	9
2,6-dimePhOH	10.59	AN	1.5	Pt	9
2,6-dimePhOH	10.59	AN + diethylamine	0.46	Pt	9
2,6-dimePhOH	10.59	MeOH + NaOH	0.20	Pt	9
Biphenol	-	AN	1.2	BPG	22
m-cresol	10.00	AN	2.4	Pt	*
m-cresol	10.00	THF	2.4	Pt	*
m-cresol	10.00	MeOH	2.4	Pt	*
m-cresol	10.00	DMF	2.4	Pt	*

* This work

Phenol molecules are adsorbed parallel to the metal surface [15] and reorient vertically when the surface coverage increases. If the substituted phenols also adsorb in the same way, then the presence of two methyl groups at the ortho position does not permit the adsorption of 2,6-dimethylphenol and, hence, the adsorption of 2,6-dimethylphenol may be weaker than PhOH. In the case of *m*C the *meta* Me group does not impose any steric restriction in the molecule, but increases the adsorption by increasing the electron density on the 'O' atom of the OH group. Hence the order of adsorbability is likely to be *m*-cresol > PhOH > 2,6-dimethylphenol.

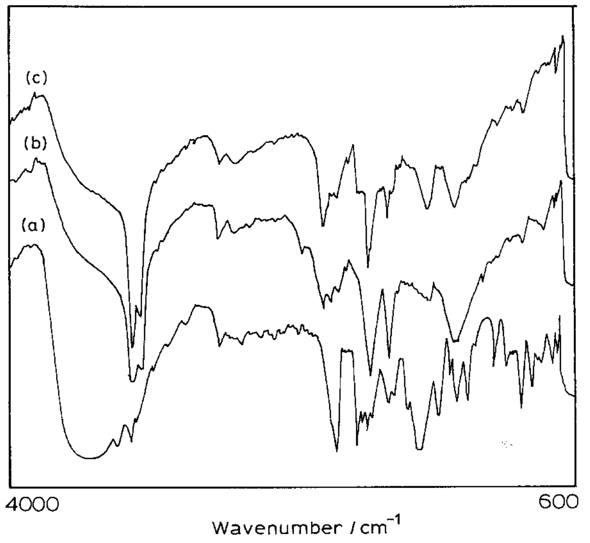
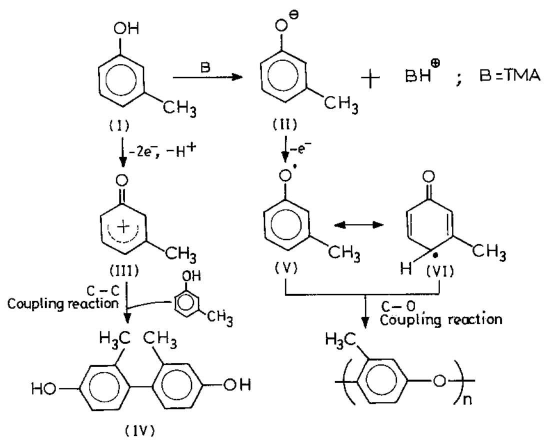


Fig. 7. Infra red absorption spectra of: (a) *m*-cresol; (b) poly(*m*C)/AN-Pt; and (c) poly(*m*C)/DMF-Pt.

In the light of earlier literature on the anodic oxidation of phenols [5,6,16–18] and on the basis of our own results, Scheme 1 may be proposed for the anodic oxidation of *m*-cresol.

The pKa (10.00) value of *m*C indicates that the equilibrium molecular *m*C(I) and dissociated 3-methyphenoxide ion (II) [19,20] is more towards molecular *m*C; the undissociated *m*C undergoes a two-electron anodic oxidation with simultaneous removal of hydrogen ion forming the phenoxonium ion (III) [20]. The phenoxonium ions are reactive electrophiles and hence a coupling reaction involving electrophilic attack of an anodically generated phenoxonium ion on the starting *m*C occurs to form the dimer (IV). On the other hand, 3-methylphenoxide ion (II), on anodic oxidation, produces the phenoxy radical (V) via a one electron removal and a C–O coupling reaction



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

*Table 3. Analytical data of poly(*mC*)* [(C$_6$H$_3$(CH$_3$)-0) (ClO$_4^-$)$_x$]

Solvent	C/%	H/%	ClO$_4^-$/%	N/%	*x*	0*
AN	56.28 (56.45)†	4.55 (4.03)	28.66	0	0.43	10.51
THF	51.45 (51.62)	4.49 (3.68)	34.70	0	0.57	9.36
CHMeOH	55.26 (55.30)	4.66 (3.95)	32.09	0	0.46	7.99
DMF	58.88 (58.90)	4.83 (4.20)	25.70	0	0.36	10.59

* Calculated by subtracting the total of C,H,N, ClO$_4^-$ composition from 100.

† Calculated compositions in parentheses.

between the phenoxy free radicals: this is expected to occur preferentially, since the phenoxy free radical is very unreactive in an electrophilic substitution reaction. Thus if *m*C is in undissociated form C–C coupling occurs primarily, and the main product is the dimer and, if it is in the dissociated form, C–O coupling occurs to form polymer.

TMA abstracts the proton from *m*C, dissociating it into 3-methyl phenoxide ion (II) (Scheme 1), which adsorbs on the metal and undergoes one electron oxidative polymerization to yield a thin film on the electrode. The different concentrations of TMA required in the various media may be due to different acid (*m*-cresol)–base (trimethylamine) equilibria in the media.

The CV runs in DMF and MeOH containing TMA (Figs. 1b and 2b) exhibited a peak corresponding to TMA oxidation (adsorption). MeOH and DMF media are not suitable for the electropolymerization of *m*-cresol, as the adsorbed TMA in these media forces the electropolymerization to take place in the vicinity of the electrode rather than on the electrode. As a consequence thick deposits are obtained (the thickness increases further with TMA concentration) (Table 1). The elemental analysis of poly(*m*C) is presented in Table 3 which reveals the absence of nitrogen.

3.5. *Properties*

3.5.1. Conductivity. The conductivity of the 'as grown' film at 298 ± 1 K measured by 4-probe technique range 10^{-10} to 10^{-8} S cm^{-2}.

3.5.2. Thermal stability. The TGA and DTA analyses were conducted from 298 to 1493 K at a linear heating scan rate of 1 K cm^{-1} (Fig. 8). The activation energy (E^*) for some of the weight loss process is calculated assuming first order kinetics. From the Arrhenius plot of $\ln k/w$ against $1/T$ (Fig. 9) where k is the rate of weight loss (in percentage of the original weight per second) at room temperature T with w as the corresponding weight (as a percentage of the original weight) of the polymer remaining, the slope is equal to $-E^*/R$. The data were evaluated over the second weight loss step, which is of greater interest.

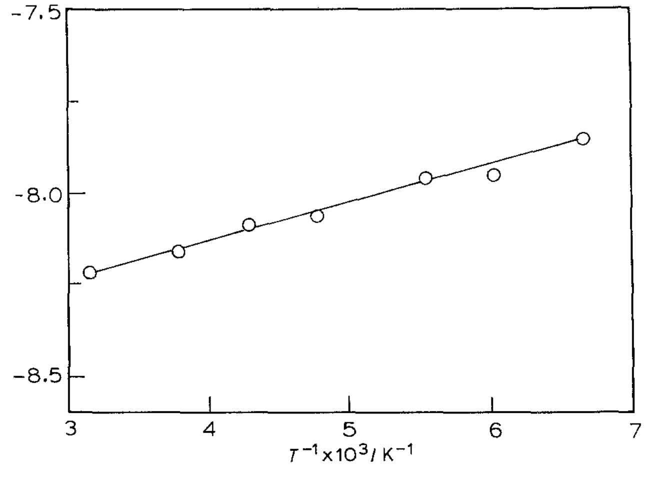


Fig. 8. Plot of $\ln(k/w)$ against $1/T$. $E^* = 6.006$ kJ mol^{-1}.

The first thermal degradation for poly(*m*C) commences with a weight loss of typically 4–6% extending from 293 K to 423 K and can be attributed to the expulsion of solvent molecules from the polymer matrix. Although co-evolution of other species may not be ruled out such losses are insignificant, compared to that of solvent over this temperature range, as the thermal analyses were performed on 'as grown' polymer.

The second weight loss occurring typically between 423 and 823 K is due to loss of dopant ClO$_4^-$. The low E^* (6 kJ mol^{-1}) calculated in this work qualitatively suggest the low pKa value of poly(*m*C). The third step starting at 823 K may be attributed to the skeletal decomposition (after the elimination of the dopant).

3.5.3. Corrosion protection. The corrosion protection offered by poly(*m*C) on copper in 1 M H$_2$SO$_4$ is presented in Table 4 which also contains various phenols subjected to similar treatment (i.e. phenols were electropolymerized according to the literature and calculated amounts were dissolved in DMSO and were sprayed over 5 × 5 cm^2 copper plates). From the amount of weight loss at definite time intervals, corrosion rates, and hence corrosion inhibition efficiencies, were calculated according to the equation

$$P = \frac{W_0 - W}{W_0} \times 100\%$$

where W_0 and W are the corrosion rates (weight loss μg cm^{-2} h^{-1}) in the absence and presence of coating and P is the corrosion inhibition efficiency [13]. It can

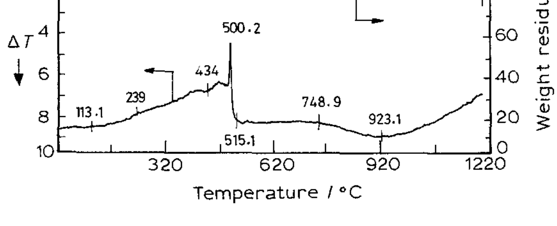


Fig. 9. Thermal analysis of poly(*m*C)/DMF.

Table 4. Corrosion inhibition characteristics of various phenols for copper in 1 M H_2SO_4 solution (5 mg of the polymer dissolved in 5 ml of DMSO was sprayed on 5 × 5 cm^2 copper)

Polymer (*Ref.*)	*Corrosion rate* /μg cm^{-2} h^{-1}	*Inhibition* /%
Untreated copper	150	–
Polyphenol [14]	128	14.67
Poly (2-allyl-phenol) [23]	42	72.00
Polyphenol [24]	34	77.33
Polyphenol [25]	30	80.00
Poly(*m*-cresol)*	40	73.33

* Prepared in AN medium and present work.

be seen from Table 4 that the phenols have almost similar inhibition efficiency.

4. Conclusions

Poly(*m*C) coatings have been successfully obtained on platinum in the presence of trimethylamine. Thick or thin coatings are obtained depending on whether TMA is adsorbed or not. The polymer obtained from DMF and AN has good corrosion protection and thermal stability and is free from the troublesome amine group.

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