

Synthesis and Characterization of Poly(*o*-ethoxyaniline): A Processable Conducting Polymer

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SYNOPSIS

The synergic effect of the substituentlike ethoxy group on the electronic properties of conducting polyaniline was investigated. The presence of substituents affects not only the electrochemical polymerization window but also brings about changes in optical and electronic properties of the parent polymer polyaniline. The study indicates that electrochemical polymerization of (*o*-ethoxyaniline) yields a conducting polymer that shows a multiple color transition (yellow → green) on switching the potential between the reduced and oxidized states with an electrochromic response time of 40 ms in addition to its solubility in dimethyl sulfoxide, *N*-methyl pyrrolidinone, etc. However, the chemical polymerization of the monomer yields a crimson red polymer that is less conducting but has solubility in ethanol/methanol. Evaluation of this alcohol soluble polymer as a corrosion inhibitor for iron in acidic medium shows that it offers corrosion inhibition efficiency of 90%. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Conducting polymers have recently attracted a great deal of attention from polymer scientists, physicists, and material scientists due to their widespread technological applications such as active electrode materials in energy storage systems,^{1,2} optoelectronic devices,^{3,4} sensors,^{5,6} and as antistatic materials.^{7,8}

Polyaniline (PANI), the polymer resulting from the oxidative polymerization of aniline, has emerged recently as one of the best candidates among conducting polymers because of its environmental stability and ease of preparation. The PANI and substituted PANIs belong to a separate class of conducting polymers whose electronic properties can be reversibly controlled by protonation. PANI is built up from reduced ($-\text{B}-\text{NH}-\text{B}-\text{NH}-$) and oxidized ($\text{B}-\text{N}=\text{Q}=\text{N}-$) repeat units, where B denotes the benzenoid and Q denotes the quinoid ring. The ratio of amine to imine yields various structures like the reduced form leucoemeraldine,

the 50% oxidized form emeraldine base, and the fully oxidized form pernigraniline. The exceptional environmental stability of conducting PANI is mainly due to the chemically flexible $-\text{NH}$ group present in the polymeric backbone flanked on either side by a phenylene ring. This $-\text{NH}$ group has very high chemical flexibility, such as protonation and deprotonation, in addition to the availability of a lone pair of electrons that can easily take part in surface adsorption phenomenon. However, many of the applications of PANI are restricted because of its unprocessability and insolubility in common organic solvents due to the extensive delocalization of π electrons. The availability of π electrons must ensure them as good corrosion inhibitors provided these polymers are made soluble in water miscible solvents like CH_3OH and $\text{C}_2\text{H}_5\text{OH}$. Recently it has been shown that PANI can be made soluble in *N*-methyl pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), and dimethyl formamide (DMF) using functionalized organic acids as dopants.⁹⁻¹¹ However, the introduction of water in these solvents precipitates the otherwise soluble PANI, thus preventing its use as a corrosion inhibitor for iron and mild steel in acidic medium. Theoretical studies on PANI¹² indicate that the bandgap and bandwidth

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Table I Yields of PEA in 1.0 M HCl Medium (25 ± 1.0 C) Using Various Oxidants

Oxidant	E°_{ox} (V)	Time (h)	Stoichiometric Ratio of Oxidant to Monomer	Polymer Yield (%)
NH ₄ S ₂ O ₈	2.0	4	1 : 1	53.9
			0.5 : 1	64.3
			0.25 : 1	32.9
K ₂ S ₂ O ₈	2.0	4	1 : 1	52.6
			0.5 : 1	60.4
			0.25 : 1	32.1
K ₂ Cr ₂ O ₇	1.33	4	1 : 1	46.4
FeCl ₃	0.77	6	0.5 : 1	51.3
			1 : 1	24.3
			0.5 : 1	12.3

are affected by the torsion angle between adjacent repeating units of the polymer chain. Thus the alkyl substituted PANI has better solubilities in organic solvents than unsubstituted PANIs, primarily because of the stereo-electronic effect of the substituent on the torsional angle.¹³ It has been reported that poly(*o*-toluidine) exhibits better electrochemical potential window and electronic properties, such as reduction in electrochromic response, in addition to the solubility in various organic solvents like DMSO, DMF, tetrahydrofuran (THF), acetonitrile (ACN), etc., that could be due to the steric effect of the substituted groups.¹⁴ However, these polymers are insoluble in water-miscible solvents like ethanol (EtOH) and methanol (MeOH). Hence, the present article reports a systematic study on the chemical and electrochemical polymerization of *o*-ethoxyaniline and characterization of the resultant soluble conducting poly(*o*-ethoxyaniline) (PEA) by spectroscopic techniques such as FTIR and UV visible, thermogravimetric analysis, and by electrochemical techniques like cyclic voltammetry and chronoamperometry. The corrosion inhibition efficiency by using alcohol-soluble polymer for iron and mild steel in acidic medium was evaluated by the linear polarization resistance method (LPR), the Tafel line extrapolation method (TLE), and direct weight loss experiments.

EXPERIMENTAL

Materials

o-Ethoxyaniline (Aldrich) was vacuum distilled before use. All other reagents used were of AR grade.

Polymerization

The polymerization of (*o*-ethoxyaniline) or *o*-phenetidine was carried out under aqueous acid conditions both by chemical oxidative polymerization and by electrochemical techniques at platinum, indium tin oxide (ITO), and stainless steel electrodes.

Chemical Polymerization

The polymerization of *o*-ethoxyaniline was carried out in an aqueous medium of pH 0–1 by using various oxidants such as ammonium persulfate, potassium persulfate, potassium dichromate, and ferric chloride. The pH of the reaction mixture was adjusted to 1 by adding either of the acids such as hydrochloric acid, sulfuric acid, sulfamic acid (SMA), or *p*-toluene sulfonic acid (PTSA). All experiments were carried out under thermostatic conditions at $25 \pm 1^{\circ}\text{C}$. The aqueous solution of oxidant was added in increments under vigorous stirring conditions. The stirring was continued to ensure the completion of the reaction. At the end of the reaction period the reaction mixture was filtered and washed thoroughly with distilled water. The polymer so obtained was dried under dynamic vacuum at room temperature for 48 h. The leached form of the polymer was obtained by treating the polymer with aqueous ammonia for 24 h, followed by filtration and thorough washing with distilled water and subsequent drying under dynamic vacuum for 48 h.

Electrochemical Polymerization

The electrochemical polymerization was carried out from 0.1 M monomer in 1.0 M protonic acid aqueous solution. Prior to polymerization, the solution was deoxygenated by passing through argon gas for 30 min. The polymerization was carried out potentiostatically at 0.75 V vs. standard calomel electrode (SCE) on either the platinum (0.25 cm²) or stainless steel electrode. The polymer growth was also studied by sweeping the potential between -0.2 to 1.0 V at a scan rate of 50 mV/s.

Table II Effect of Protonic Acid on PEA Yield

Medium	pK	Polymer Yield (%)
HCl	-7.0	64.3
H ₂ SO ₄	-4.0	58.6
NH ₂ SO ₃ H	1.04	69.8
H ₃ C · C ₆ H ₄ · SO ₃ H	—	66.1

o-Ethoxyaniline = 0.1M; (NH₄)₂S₂O₈ = 0.1M; Temp. = $25^{\circ} \pm 1^{\circ}\text{C}$.

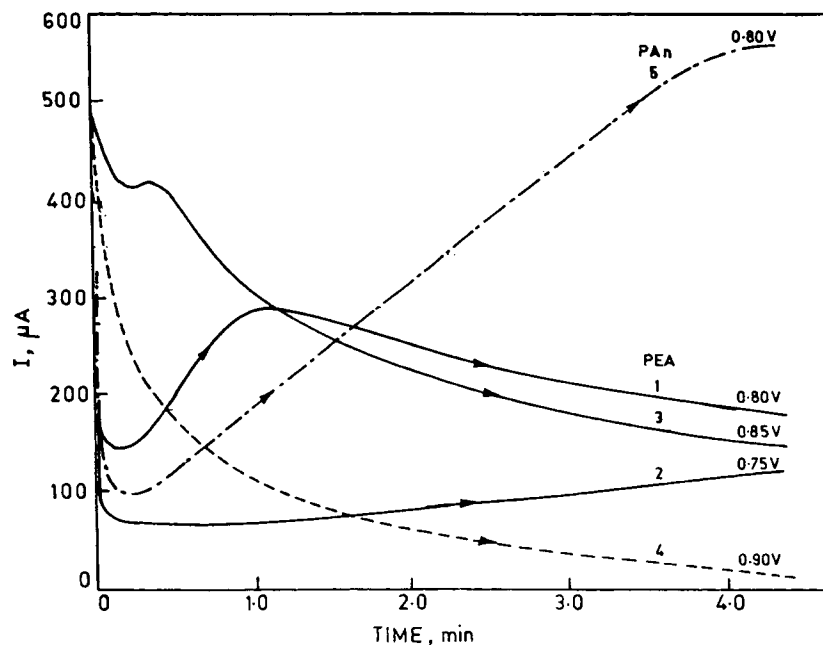


Figure 1 Current time transients for the potentiostatic growth of PEA at different potentials (curves 1–4) on platinum electrode vs. SCE; curve 5, potentiostatic growth of polyaniline at 0.8 V on Pt electrode vs. SCE.

Characterization

The characterization of the polymer was carried out by spectroscopic as well as by electrochemical techniques. Infrared (IR) spectra of the doped and compensated polymer were recorded on a Nicolet FTIR spectrometer using a KBr pellet. The electronic spectra of the soluble polymer were recorded on a Hitachi U-3400 spectrophotometer. The X-ray diffraction powder pattern of PEA was recorded using $\text{CuK } \alpha, \lambda$ of 1.5418 Å on a JEOL JDX 8030 X-ray diffractometer. Thermogravimetric analyses of the doped and leached polymer were recorded on a Perkin Elmer 7 thermal analyser. Nitrogen was used as the purge gas and the heating rate was 20°C/min. The chronoamperometric studies of the PEA film obtained by the potentiostatic technique was carried out on a Bio-analytical system (BAS 100 A) by switching the potential between –0.2 and 0.6 V to –0.2 V vs. SCE. The cyclic voltammetric studies were carried out using a Tacussel bipotentiostat coupled with an X-Y recorder (BBC, Model SE 780) and universal programmer PARC 175.

Soluble Polymer as Corrosion Inhibitor

The evaluation of the soluble conducting polymer as a corrosion inhibitor was carried out by the electrochemical techniques TEM and LPR, as well as

by the direct weight loss method. For these electrochemical experiments a three electrode cell with 1 cm² of iron embedded in an araldite mold was used as a working electrode, SCE as the reference electrode, and platinum foil as the counter electrode. The working electrode was polished with 1/0, 2/0, 3/0, and 4/0 emery papers and degreased with trichloroethylene before use. Before starting the electrochemical experiments for corrosion testing, the test sample was allowed to reach steady state after immersion in the cell for 15 min.

RESULTS AND DISCUSSION

Chemical Synthesis

The chemical oxidative polymerization of *o*-ethoxyaniline is carried out under aqueous conditions (pH ≈ 0–1) in the presence of protonic acids such as hydrochloric acid, sulfuric acid, SMA, and PTSA, using various oxidizing agents like ammonium peroxydisulfate, potassium peroxydisulfate, potassium dichromate, and ferric chloride. The yield of polymer using various oxidants in HCl medium are tabulated in Table I. The HCl medium was chosen for the study because HCl is the preferred medium for PANI synthesis as well as for corrosion studies of metals. As can be seen from Table I, the yields of PEA varied

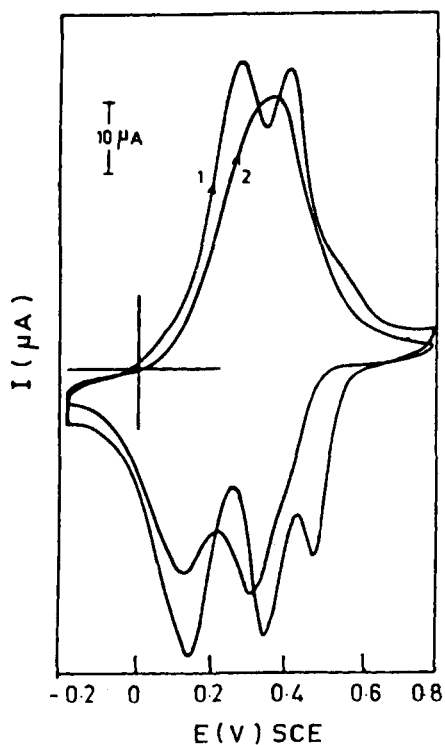


Figure 2 Cyclic voltammogram of PEA in (1) sulfuric acid medium (2) sulfamic acid medium.

markedly with the oxidation potential of the oxidant. The higher molar ratio of oxidizing agent (M_{ox}) yields a low polymerization efficiency whereas $M_{ox}/M_{ea} = 0.5$ provides a better polymer yield. This implies that higher M_{ox} may lead to the formation of a large fraction of water soluble dimers and oligomers, possible by causing oxidative degradation of the polymer formed during the reaction. The reason for lower polymer yields with $K_2Cr_2O_7$ as oxidant is that the oxidation of *o*-ethoxyaniline to PEA is a 2F reaction whereas dichromate to Cr^{3+} is a 6e

Table III Redox Potential of PANI and Its Derivatives (vs. SCE)

Polymer	Medium	Epa	Epa	ΔE_p	Reference
		(V) I	(V) II	(V) II-I	
PEA	H_2SO_4	0.28	0.42	0.14	This work
	SMA ^a	0.29	0.36	0.07	This work
PMA	HCl	0.22	0.41	0.19	17
	SMA	0.23	0.40	0.177	17
P(<i>o</i> -tol)	H_2SO_4	0.24	0.5	0.26	14
PANI	H_2SO_4	0.09	0.63	0.54	18
	SMA	0.125	0.67	0.545	18

^a Scan rate of 10 mV/s.

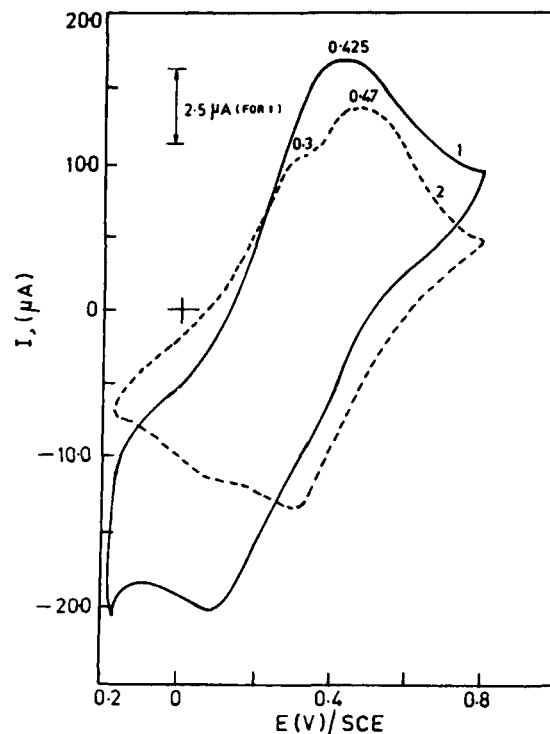


Figure 3 Cyclic voltammogram of chemically synthesized PEA film on platinum electrode cast by evaporation: (· · ·) green form, (— —) red form.

change reaction. This implies that one dichromate ion can oxidize three molecules of *o*-ethoxyaniline to give cation radicals, unlike persulfate where one persulfate anion can oxidize only one *o*-ethoxyaniline molecule, possibly because this $Cr_2O_7^{2-}$ oxidation accelerates the formation of oligomers and hence the polymerization yield is lowered. As is evident from Table I, when using ammonium peroxydisulfate as oxidant, the polymer yield is better and hence the study was also undertaken to investigate the yield of PEA in the presence of various acids using ammonium peroxydisulfate as oxidant. Results of the study are tabulated in Table II. The yield in the presence of SMA is higher because SMA itself cat-

Table IV Soluble Fraction (%) of Polymer

Polymer	MeOH	EtOH	$(CH_3)_2CO$	DMSO	DMF
PANI doped	0	0	0	0	0
PANI undoped	0	0	0	20	19
PMA doped	16	15	12	58	62
PMA undoped	35	23	21	78	79
PEA doped	72	73	70	98	99
PEA undoped	74	75	72	99	99

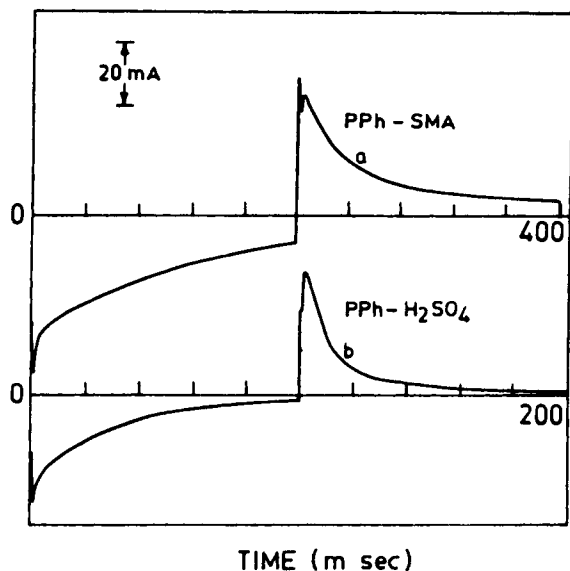


Figure 4 Chronoamperometric response of PEA film in (a) SMA medium and (b) H_2SO_4 medium. Experimental conditions: initial $E = -200$ mV, high $E = 400$ mV, low $E = -200$ mV; pulse width = 200 ms for (a) and 100 μs for (b).

analyzes the polymerization reaction as SMA exists in the following principal equilibrium:



This equation depicts the principal equilibrium whereas various species like NH_2SO_3^- , NH_2^+ , $\text{NH}_3^+\text{SO}_3^-$, $\text{NH}_3^+ : \text{SO}_3^-$ also exist along with the principal equilibrium.¹⁵ The existence of free radicals and radical ions makes SMA the best catalyst in the polymerization of *o*-ethoxyaniline.

Electrochemical Polymerization by Potential Step Technique

The electrochemical polymerization of *o*-ethoxyaniline in 1.0M SMA/1.0M H_2SO_4 medium is carried out by the potential step technique on a platinum electrode (0.25 cm^2) vs. SCE. The current-time transients are plotted to various potential steps in order to establish the growth mechanism of the polymer PEA. At 0.7 V vs. SCE, no polymerization occurs. At 0.8 V (Fig. 1), the $i-t$ transient shows that initially in the first few seconds, the current falls rapidly due to the adsorption of the monomer on the electrode surface and then slowly current increases to maximum value due to oxidative polymerization of adsorbed monomer. With the increase in the thickness of the polymer film due to the ohmic drop, a slow fall in current is observed. This $i-t$ re-

sponse exhibits a similar behavior as polypyrrole where the relationship for progressive nucleation has been established from the $I = f(t)$ curve¹⁶ by analogy with the metal electrodeposition. Similarly on increasing the potential step to 0.85 V, the $i-t$ transient is observed as shown in Figure 1, curve 3 that implies that adsorbed monomers are readily polymerized as indicated by a rapid increase in current up to 20 s, followed by a decrease in current. At this point red coloration develops in the solution (due to overoxidation). However, at potential > 0.9 V vs. SCE, no increase in current is observed but a rapid fall in current is observed followed by red colored polymer diffusing into the solution. At 0.75 V vs. SCE, the growth of polymer does occur but a slow regular increase in current is observed. This implies a uniform deposit of the polymer on the electrode surface. However, in this case no red coloration is observed even after prolonged electrolysis and thus the polymer deposited on the electrode surface is dark green. This observation suggests that if the polymer is grown at a potential greater than 0.8 V, the polymer gets overoxidized, which is less conducting. However, the IR spectral studies do not differentiate much on the overoxidized red polymer and green conducting

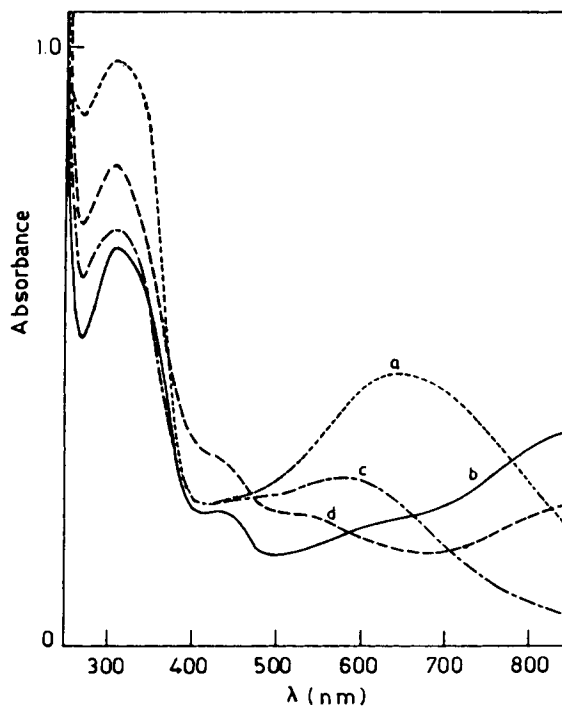
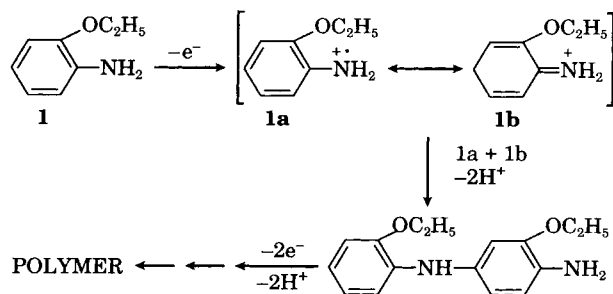


Figure 5 UV-visible absorption spectra (after removing alcohol-soluble portion) of (a) leached PEA solution in DMSO; (b) HCl doped PEA solution in DMSO; (c) leached PEA solution (PEA synthesized from SMA medium); (d) SMA-doped PEA.

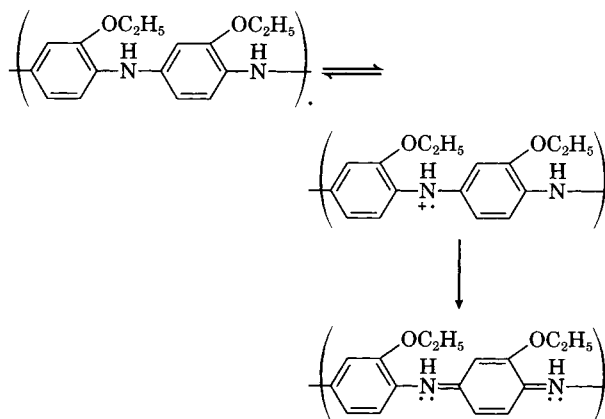
Table V Absorption Bands Observed in UV-vis. Solution Spectra in PEA

System	Method of Preparation	λ_{\max} (nm) Alcohol Soluble	λ_{\max} (nm) DMSO Soluble
PEA-HCL	Chemical Electrochemical	281, 302, 451, 502	310, 434, 827
PEA leached	Chemical Electrochemical	280, 304, 491 —	310, 634 320, 614
PEA-SMA	Chemical	304, 452, 506	304, 435, 832

polymer. The only difference in IR is the absorption band due to the —B—Q—B— band that shows that bands due to the benzenoid structure are completely missing in the red form polymer. Therefore, the best polymerization potential for the polymerization of *o*-ethoxyaniline is between 0.7 and 0.8 V vs. SCE and is hence due to the narrow range of polymerization potential and sensitivity toward overoxidation (as is evident from the red coloration in solution). This suggests that the polymer is directly in contact with the electrolyte and goes to the quinoid form (as is also evident from the UV-visible spectra) if the upper limit of the electrode potential is kept ≥ 0.85 V. The quinoid structure, the highly oxidized form of PEA, has few charge carriers and is less conductive compared with the green form of the polymer. In almost all the polymerization reaction the oxidation potential of the polymer is less than the polymerization potential of the monomer and hence prolonged electrolysis leads to the overoxidation of the polymer rather than the formation of polymer. Under such conditions soluble oligomers diffuse out into the solution. Polymerization occurs via the formation of a radical cation of the monomer near the vicinity of the anode surface. The mechanism of the electrochemical polymerization of *o*-ethoxyaniline is believed to proceed via a radical cation formation that reacts with a second radical cation to a dimer. This reacts further with the radical cation of the monomer to build up the polymer chain. A possible reaction mechanism can be written as:



The electrochemical polymerization of *o*-ethoxyaniline leads to formation of two different polymers with different spectral and electrochemical properties. The polymer layer in direct contact with the electrode surface is green whose cyclic voltammogram (Fig. 2) in H_2SO_4 medium is almost similar to the parent polymer, PANI with the difference that the protonation peak (II) of PAN at 0.7 V shifts to a lower potential value and peak (I) due to surface electron transfer shifts to higher potential value. However, in the cyclic voltammogram of the polymer film in SMA medium, both peaks merge and give one broad peak (0.32 V) at a sweep rate of 50 mV/s, implying that electron transfer and protonation occurs almost simultaneously. This implies that the diamine is directly oxidized to diimine and there is no observable degradation of the polymer which can be presented as:



However, the cyclic voltammogram of PEA at a scan rate of 10 mV/s in sulfamic acid medium again gives two peaks at 0.29 and 0.36 V vs. SCE. The polymer in contact with the electrolyte has a red color whose cyclic voltammetric response (after evaporating CH_3OH soluble polymer on the Pt electrode) gave only one peak at 0.425 V vs. SCE. This red polymer is the overoxidized form of green PEA. This red form acts as a protective layer for the green

form and is much less conducting as is evident from the current-time transients. The redox potential values of the various substituted PANIs and of PANI are given in the Table III. The perusal of Table III reveals that oxidation peak potentials are dependent upon the nature of the substituents. The introduction of electron donating substituents on the aromatic ring has a favorable effect on the reduction of oxidation potential of monomer as well as of polymer¹⁹; however, if degree of conjugation is less, then the redox potential of polymer will be different than expected. Therefore, a positive shift in redox potential is observed for the first oxidation reaction of substituted PANIs compared to PANI while the last oxidation peak is shifted to lower potential. The electronic effects of the substituents cannot explain the positive shift of the first oxidation potential and consequently the steric effects as well as electronic effects of the substituents have to be taken into account. In fact, it has been reported that the presence of bulky substituents can induce some nonplanar conformations that decrease the conjugation along the polymer backbone and are responsible for higher oxidation potential.²⁰ Therefore, on the basis of a positive shift of the first oxidation peak, higher torsional angles are expected in reduced substituted PANIs similar to those observed in poly(*o*-toluidine) rather than in the unsubstituted PANI radical cation's contribution due to the electron donating property of alkyl and alkoxy substituents leading to the negative shift of the last oxidation peak potential value. Therefore, lowering of peak potential difference (ΔE) in the PEA with respect to PANI may be rationalized by considering the steric effects of the substituents that may induce some ring twisting with consequent reduction in π conjugation in the polymer chain, thereby destabilizing the polysemiquinone radical cationic form of the polymer. This suggests that the stability of the polysemiquinone radical cation is decreased in the substituted derivative to the extent that the reduced amine form of the polymer is directly oxidized into the imine form and that the semiquinone form has no detectable existence under the conditions employed in cyclic voltammetry studies. Once a radical cation forms, the second electron oxidation to the quinonediimine can be facilitated by the formation of two fully sp^2 hybridized nitrogens that could relieve some steric strain²¹ due to the lowering of the bond angles at the imine nitrogen, thereby causing a shift of second oxidation potential to lesser value.

Electrochemical Behavior of Chemically Synthesized Polymer

To better understand the characteristics of the polymer PEA, the electrochemical response of the chemically synthesized polymer was also recorded and is given in Figure 3. The chemically prepared polymer is completely soluble in DMSO, DMF, and NMP; however, 75% of the polymer is soluble in methanol, ethanol, etc., giving a red-colored solution. The alcohol-insoluble portion of the polymer has a bottle green color and is completely soluble in DMSO. Two separate electrochemical investigations on the alcohol-soluble and -insoluble portion were carried out. The red polymer film on the electrode surface was obtained on the Pt electrode by evaporating an alcohol solution and green polymer film by evaporating the alcohol-insoluble portion of the polymer in DMSO. The cyclic voltammetric response of both the polymer films were identical to the electrochemically synthesized polymer film, suggesting that the electrochemically and chemically prepared polymers lead to the same end polymer via an identical mechanism.

Solubility of PEA

The ethoxy group attached to the aniline ring at the *ortho* position increases the solubility of the polymer in organic solvents as compared to PANI as can be seen from Table IV. The solubilization of PEA has opened up a new area for its use as an antistatic conducting coating as well as application as a corrosion inhibitor. The alcohol-soluble portion has been evaluated for its application as a corrosion inhibitor for iron under acidic conditions. The DMSO-

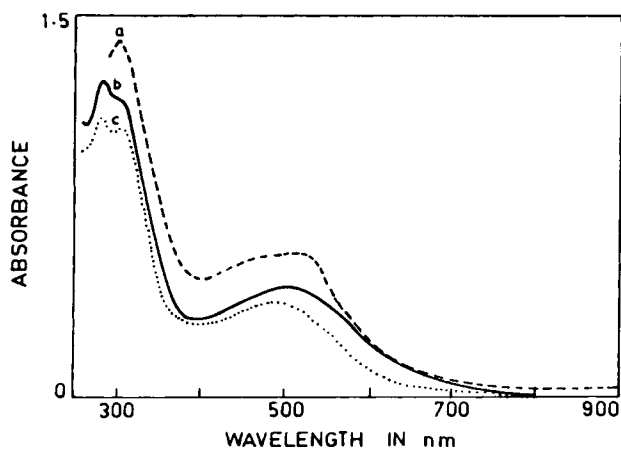


Figure 6 UV-visible solution spectra of alcohol-soluble PEA: (a) SMA-doped PEA; (b) HCl-doped PEA; (c) compensated PEA.

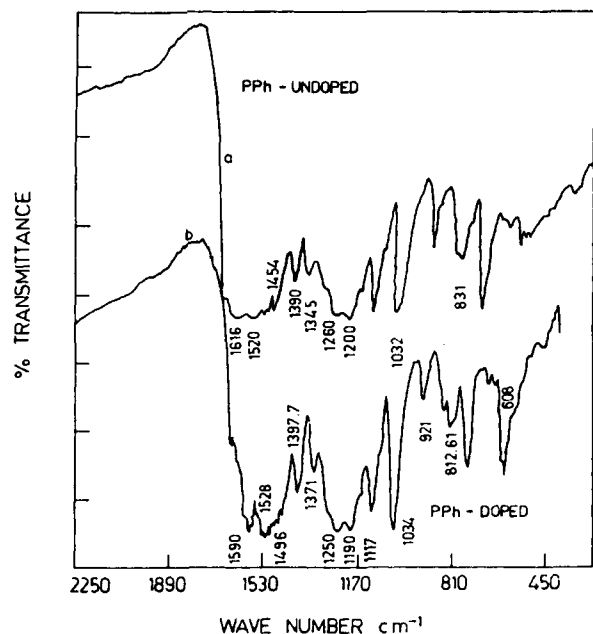


Figure 7 FTIR spectra of alcohol-soluble crimson red form of PEA in KBr: (a) leached PEA and (b) doped PEA.

soluble portion was not tested however for corrosion inhibition efficiency studies because of precipitation of the polymer when DMSO solution is added to the aqueous acidic solution.

Chronoamperometric Studies

PEA film on a platinum electrode (0.25 cm^2) prepared by passing a charge of 0.30 C/cm^2 in sulfuric acid and SMA medium exhibits electrochromic behavior on switching the potential between -0.2 and $+0.4$ to -0.2 V vs. SCE. These changes correspond to different oxidation states of PEA. Figure 4 shows the electrochromic response of an $\approx 1\text{-}\mu\text{m}$ thick polymer film in $1\text{M SMA}/1\text{M H}_2\text{SO}_4$ medium. In the reduced state (-0.2 V) this film has a golden yellow color and becomes green at 0.3 V vs. SCE. Increasing the potential above 0.4 V produces dark blue forms. The golden yellow to green transition is attributed to the oxidation of aromatic amine nitrogen to the stable radical cations; the second oxidation to dication induces a green to blue color transition. The difference in response time for oxidizing (40 ms) and reducing (60 ms) can be explained by the different electrical conductivities of the two states. Moreover, the response time of the polymer film on going from the reducing to the oxidizing state in 1.0M SMA and $1.0\text{M H}_2\text{SO}_4$, was also found to be different. The difference in response time is essentially due to the difference in the diffusing out

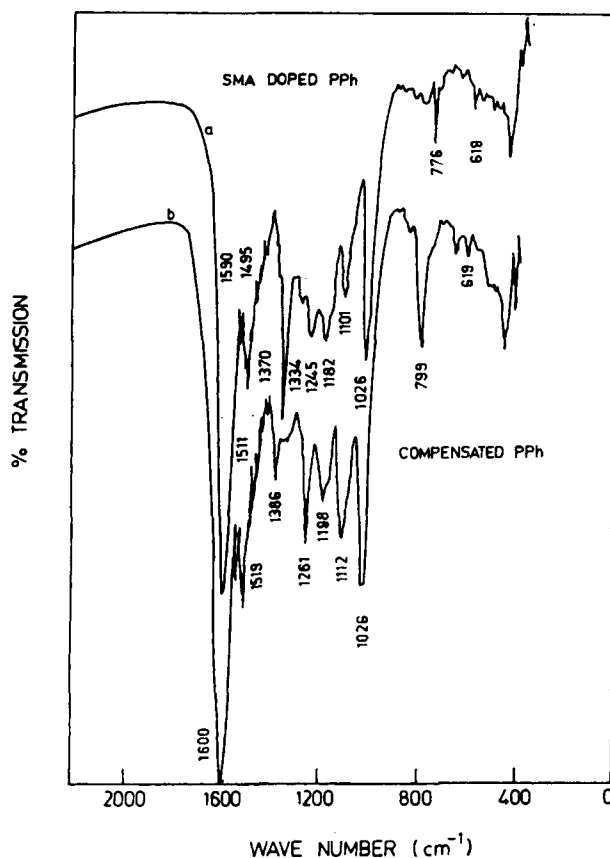


Figure 8 FTIR spectra of alcohol-insoluble form of PEA in KBr: (a) SMA-doped PEA and (b) compensated PEA.

and in of the dopant in the polymer film or the change in the hydrophilic or hydrophobic property of the polymer film. A life cycle test of the PEA film in $1.0\text{M H}_2\text{SO}_4$ medium shows that on restricting the upper potential limit to $+0.4 \text{ V}$, only 5% loss in the electrochemical activity of the polymer film is observed after 1×10^4 cycles (cycle duration 1.2 s). Therefore, attaching a substituent on the aromatic

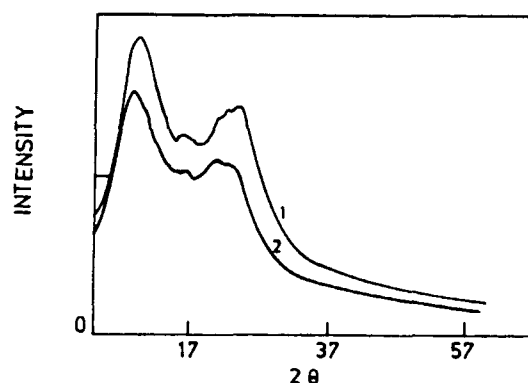


Figure 9 X-ray diffraction powder patterns of (1) SMA-doped PEA and (2) leached PEA.

Table VI X-Ray Diffraction Pattern ($\text{CuK}\alpha, \lambda = 1.5418 \text{ \AA}$)

PEA-SMA (DMSO Soluble)		PEA Undoped		PEA-SMA (Alcohol Soluble)		PEA Undoped	
2θ	d	2θ	d	2θ	d	2θ	d
7.8	11.2	7.7	11.47	7.3	12.10	6.9	12.8
10.5	8.4	10.9	8.11	8.7	10.15	8.4	10.5
20.3	4.3	21.8	4.07	22.2	4.0	11.1	7.9
24.1	3.69	23.7	3.75	24.1	3.69	16.4	5.4
						19.1	4.64

ring shows a favorable effect on the electrochromic response time and improves cycle life.

UV-Visible Spectra

As pointed out in the foregoing discussion that the polymerization of *o*-ethoxyaniline yields two type of polymers, both of them are soluble in DMSO, NMP, etc., but 75% of the polymer is soluble in ethanol/methanol. A DMSO solution of HCl-doped polymer (after completely removing alcohol-soluble portions) is green in color and gave absorption bands at 310 ($\pi-\pi^*$ transition), 434, and 827 nm (Fig. 5) that are due to the optical absorption of the metallic polaron bands of the conducting form. The hypsochromic shift of the $\pi-\pi^*$ transition and bathochromic shift of the polaron band transition as compared to PANI²² shows the decreased conjugation caused by the *ortho*-ethoxy group. Moreover, the electronic effects exerted by the $-\text{OC}_2\text{H}_5$ group leads to an increase in phenyl ring torsional angle because of the steric repulsion between the OC_2H_5 group and the

hydrogen on the adjacent phenyl rings. However, on removal of dopant, the polymer solution in DMSO (blue in color) gave absorption bands at 310 and 634 nm [Fig. 5(b)]. A similar observation is made for polymer doped with SMA and are given in Table V. However, the solution spectra of the electrochemically prepared polymer in DMSO shows absorption bands at 318, 428, and 843 nm whereas the compensated form shows bands at 320 and 614 nm (Table V). The red shift in the absorption band ($\pi-\pi^*$ transition) of the electrochemically prepared polymer to the chemically synthesized polymer shows the better conjugation in the former.

The ethanol-soluble polymer (blood red color) solution gave absorption bands at 304, 452, and 506 nm when doped with SMA; on HCl doping these bands are observed at 281, 302, 451, and 502 nm (Fig. 6). However, on removal of the dopants, the absorption bands are observed at 280, 304, and 490 nm. The band at 506 nm in PEA-SMA and 502 nm in HCl-doped PEA shows that the polymer is composed of more quinoid structure compared to green

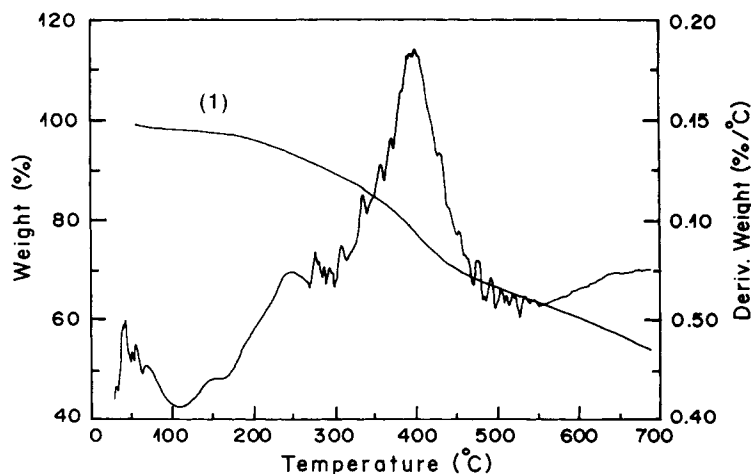


Figure 10 Thermogravimetric analysis curves of (1) SMA-doped PEA and (2) leached PEA.

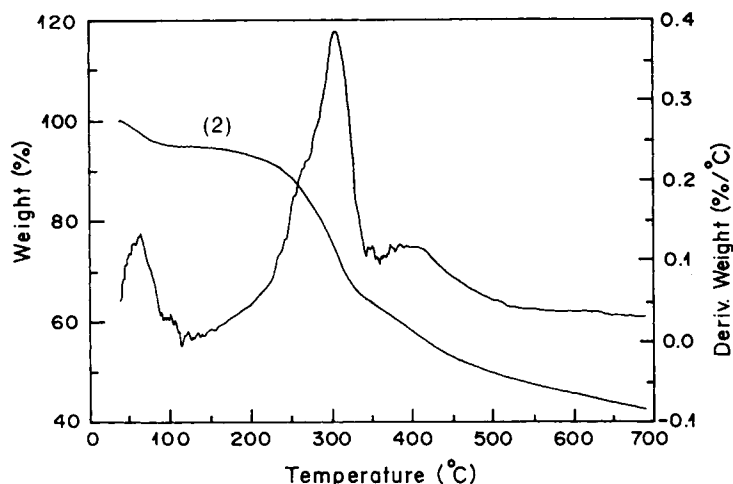


Figure 10 (Continued from the previous page)

form of the polymer. This observation is also evident from the IR spectral studies. A similar observation is also made on overoxidation of PANI due to the formation of pernigraniline with an absorption band at 530 nm.²³

IR Spectra

The FTIR absorption spectra in KBr for the red and green forms of the polymer in its doped and compensated states are given in Figures 7 and 8. The principal difference in the IR spectra of the green and red forms is the absence of the absorption band at 1490 cm^{-1} in the red form due to N—B—N; in the green form the bands for N—B—N at 1519 and 1490 cm^{-1} are characteristic of nitrogen quinoid and benzenoid (BQB) and are observed due to the charge on the polymer backbone. These bands show a blue shift from 1590 to 1600 cm^{-1} and 1490 to 1519 cm^{-1} on removal of dopant from the polymer. These changes are indicative of the conversion of the benzenoid ring to the quinoid rings in the polymer matrix. IR spectra thus suggest that the red form has less percentage of benzenoid rings. The absorption band at 1345 cm^{-1} in the overoxidized form of PANI (pernigraniline)²⁴ has been reported as characteristic to the —CN band stretch in the QBQ sequence. The 1345 cm^{-1} band in the red polymer can be assigned to the —CN bond stretch in the quinoid benzenoid sequence. It is interesting that ethoxy substitution at the two position has stabilized the overoxidized form of the polymer. However, it was very difficult to assign bands for —SO₃ stretching vibration in the present system as the involvement of the sulfamate anion

in the polymer may give rise to complex bands that may have a cumulative effect on the other IR bands.

X-ray Diffraction Pattern

Figure 9 shows the X-ray diffraction pattern of the leached PEA and PEA doped with SMA. In all cases, broadening occurs indicating the amorphous nature of the polymer. The 2θ and d values are recorded in Table VI. However, in the present case, alcohol-soluble red polymer has a far better crystallinity than the conducting green form.

Thermal Stability of PEA

Figure 10 shows the thermogravimetric curve of the undoped polymer indicating negligible weight loss ($\approx 3\%$) up to 210°C ; from 210° to 410°C , the loss in weight is 25% indicating possible decomposition of the polymer backbone. In the doped polymer, the first weight loss ($\approx 4\%$) is observed up to 80°C , possibly due to the moisture content entrapped in the polymer matrix. From 80° to 200°C , the weight loss is 3% indicating the stability of the polymer matrix. From 200° to 330°C , the weight loss is 29% corresponding to the weight of the dopant. Unlike undoped polymer, the degradation in the doped polymer is continuous, possibly due to the decomposition of the polymeric backbone.

Evaluation of Alcohol-Soluble PEA as Corrosion Inhibitor

The aromatic compounds and amines are invariably used as corrosion inhibitors because of their strong

Table VII Corrosion Inhibition Efficiency of Alcohol-Soluble PEA for Iron in 1.0M HCl

Inhibitor	Concentration (ppm)	Tafel Extrapolation Method			LPR Data		Direct Wt Loss Data	
		E_{corr} (mV)	i_{corr} (mA/cm ²)	IE (%)	Rp (ohm/cm ²)	IE (%)	Wt Loss (mg/10 cm ²)	IE (%)
Without inhibitor	—	-500	5.40	—	25	—	11.05	—
Aniline	1000	-497.5	405	15	33.3	25	7.56	32
	10000	-495.0	250	54	50.0	50	5.72	48
	20000	-495.0	220	59	54.1	54	3.71	66
<i>o</i> -Ethoxyaniline	1000	-497.5	500	17	29.2	14	8.73	21
	10000	-497.5	180	67	91.7	73	3.18	71
	20000	-497.5	68	87	275.0	90	1.65	85
PEA (alcohol soluble)	10	-500.0	290	46	62.5	60	6.63	40
	50	-493.5	85	84	175.0	86	2.04	82
	100	-485.0	72	86	275.0	91	1.73	84
	200	-492.5	62	89	325.0	92	1.2	89
PEA leached	10	-490.0	220	59	125.0	80	4.18	62
	25	-482.5	68	87	200.0	88	1.47	87
	50	-480.0	59	89	250.0	90	1.27	89
	75	-482.5	59	89	320.0	92	0.87	92
PEA-SMA doped	10	-482.5	85	84	175.0	86	2.10	81
	25	-487.5	78	86	225.0	89	1.86	83
	50	-487.5	62	89	230.0	90	1.30	88
	75	-490.0	58	90	234.6	90	0.73	93

adsorption on the metallic surface due to the presence of π electrons. However, inhibition efficiencies using monomers are not very high because of Van der Waal's repulsion between neighboring monomeric units, thus leaving the majority of the surface unprotected. We envision that soluble PEA polymer having quaternary ammonium nitrogen and π electrons from the aromatic nucleus would help in strong adsorption of polymer on the iron surface to give uniform coverage by minimizing Van der Waal repulsive forces so that maximum metal surface can be covered. From the literature²⁵ we also know that the adsorption takes place via the functional N atom of the inhibitor molecule vertically oriented to the metal surface, or it may be through the delocalized π electrons with the aromatic ring parallel to the electrode surface. Therefore, we project that the *ortho* ethoxy group attached to the polymer would be facing the electrolyte to prevent the hostile ions from reaching the iron surface to protect it from corrosion. The corrosion inhibition efficiency using various concentrations of monomer and alcohol-soluble polymer are recorded in Table VII. These findings are confirmed in the capacitance study where it was observed that even at -300 mV vs. SCE, the desorption in the cathodic region indicates the strong adsorption due to positively charged polymer on the

surface.²⁶ As Table VII reveals, such behavior is not observed when monomer is used as the corrosion inhibitor.

CONCLUSIONS

It has been shown that *o*-ethoxyaniline can be polymerized to PEA both by chemical and electrochemical synthesis to yield two types of polymers with different electrochemical and spectroscopic properties. The green, highly conducting form of the polymer, shows an electrochromic response time of 40 ms and is soluble in DMSO and NMP from which thin films can be cast. The red form of the polymer is soluble in methanol/ethanol and offers a corrosion inhibition efficiency of 90% for mild steel in 1M HCl medium.

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