Influence of Molecular Weight of Poly(*ortho*-ethoxyaniline) on the Corrosion Inhibition Efficiency of Mild Steel in Acidic Media

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ABSTRACT: The present work revealed that the chemical polymerization of *ortho*-ethoxyaniline yields two types of polymers not only with different spectroscopic properties but also with different molecular weights: (1) a green form, which corresponds to the high molecular weight fraction of the polymer with a molecular weight of 800,000 g mol^{-1} based on the polystyrene calibration. It is mainly composed of quinoid and benzoid structures, which is an indication of a half-oxidized polymer (emeraldine). This form of the polymer is insoluble in water-miscible solvents like ethanol and methanol and thus cannot be tested in terms of corrosion inhibition efficiency; (2) a red form, which corresponds to the low molecular weight fraction of the polymer with a molecular weight of 44,000 g mol^{-1}. It is composed mostly of quinoid structures and exhibits an oxidation state similar to that of the completely oxidized polymer (pernigraniline). In our case, the polymer fraction, which is soluble in alcohol, was first tested as a corrosion inhibitor for mild steel in acidic media, not only at conventional molecular weight (44,000 g mol^{-1}) but also at different molecular weights. These different molecular weights of the polymer were obtained by adding varying amounts of neutral salt to the synthesis environment. Next, the effect of the molecular weight of the red form of the polymer on the corrosion inhibition efficiency of mild steel in hydrochloric acid solutions was investigated. The obtained results showed that the adsorption of the polymer alcoholic form obeys a Temkin adsorption isotherm with no significant change as function of inhibition efficiencies for a series of molecular weights ranging from13,000 to 124,000 g mol^{-1}. The effect of temperature on the corrosion behavior of mild steel in 1*M* HCl with addition of 100 ppm of the alcoholic form of poly(*ortho*-ethoxyaniline) was studied in the temperature range 25–60°C. The associated activation corrosion energy was determined. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1275–1284, 2004

Key words: poly(*o*-ethoxyaniline); corrosion inhibition; adsorption; molecular weight; Temkin isotherm

INTRODUCTION

Research on organic corrosion inhibitors has been mainly focused on the inhibitor structure relationship with its adsorption properties and mechanism. It has been observed that the adsorption acutely depends on specific physicochemical properties of the inhibitor molecule such as functional groups, steric factors, aromacity, electron density at the donor atoms, and π-orbital character of donating electrons.[1,2] It also depends on the electronic structure of the molecules.[3,4] Furthermore, it has been noticed that both the molecular area[5] and molecular weight[6] of the inhibitor are of key importance.

Corrosion inhibition of mild steel in acidic media using poly(*ortho*-ethoxyaniline) (POEA) has been extensively studied,[7,8] although the inhibition efficiency has been obtained for only one molecular size. In fact, there is no mention in the literature of the use of POEA as a corrosion inhibitor with different molecular weights.

Therefore, the aim of the present investigation was to highlight the effect of the molecular weight of the alcoholic form of POEA on the corrosion inhibition efficiency of mild steel in hydrochloric acid solutions.

The procedure followed to produce high and low molecular weight of POEA was that described by Mattoso.[9,10]

Finally, the obtained inhibition efficiencies were further measured by the electrochemical techniques of electrochemical impedance spectroscopy and potentiodynamic polarization curves.

EXPERIMENTAL

Materials

ortho-Ethoxyaniline (Fluka Chemie, Buchs, Switzerland) was distilled under reduced pressure before polymerization. *N,N*-Dimethylformamide (DMF; HPLC-

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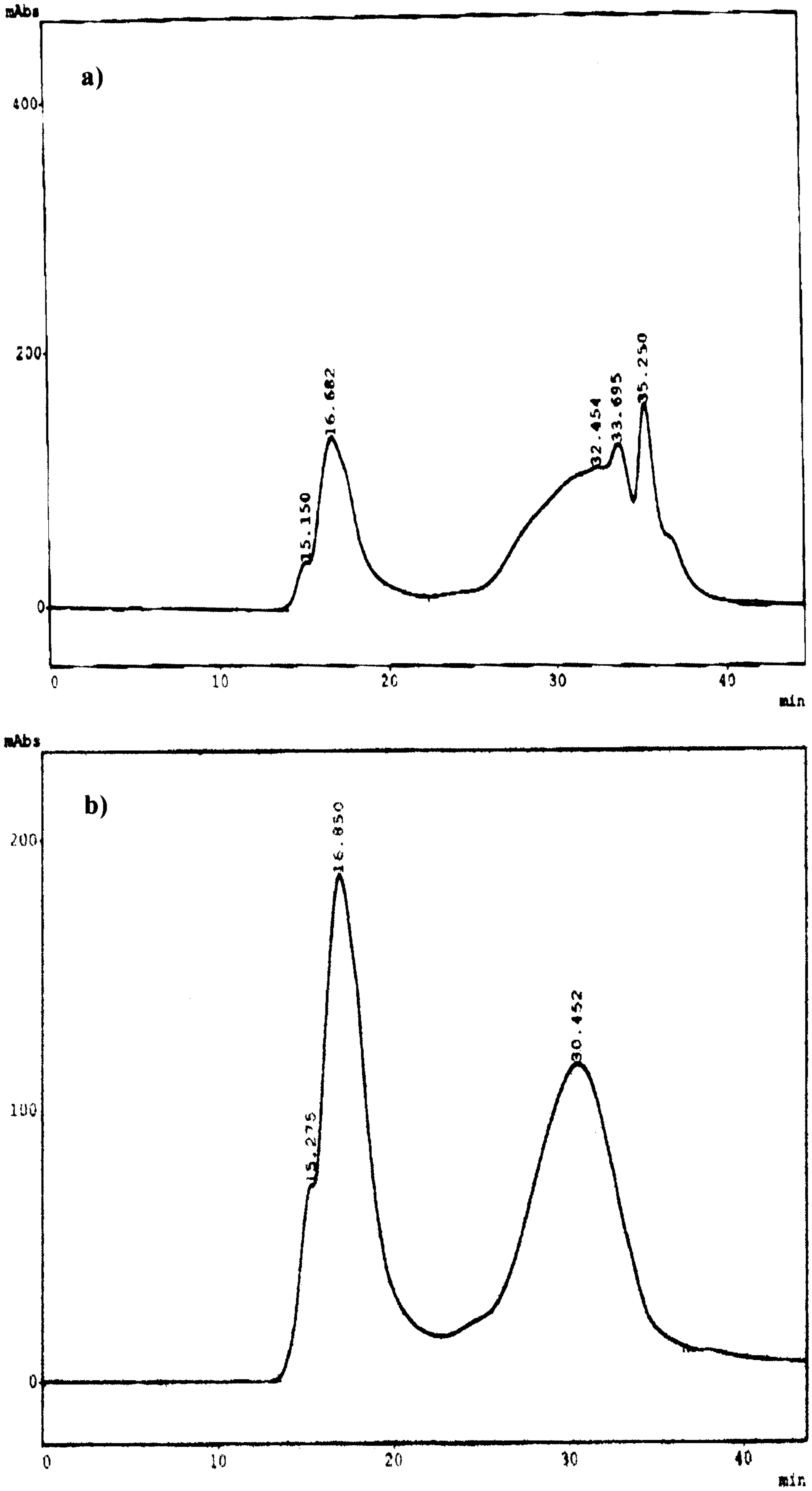

Figure 1 Gel permeation chromatogram of the chemically synthesized POEA: (a) leached POEA; (b) alcohol-insoluble form; (c) alcohol-soluble form.

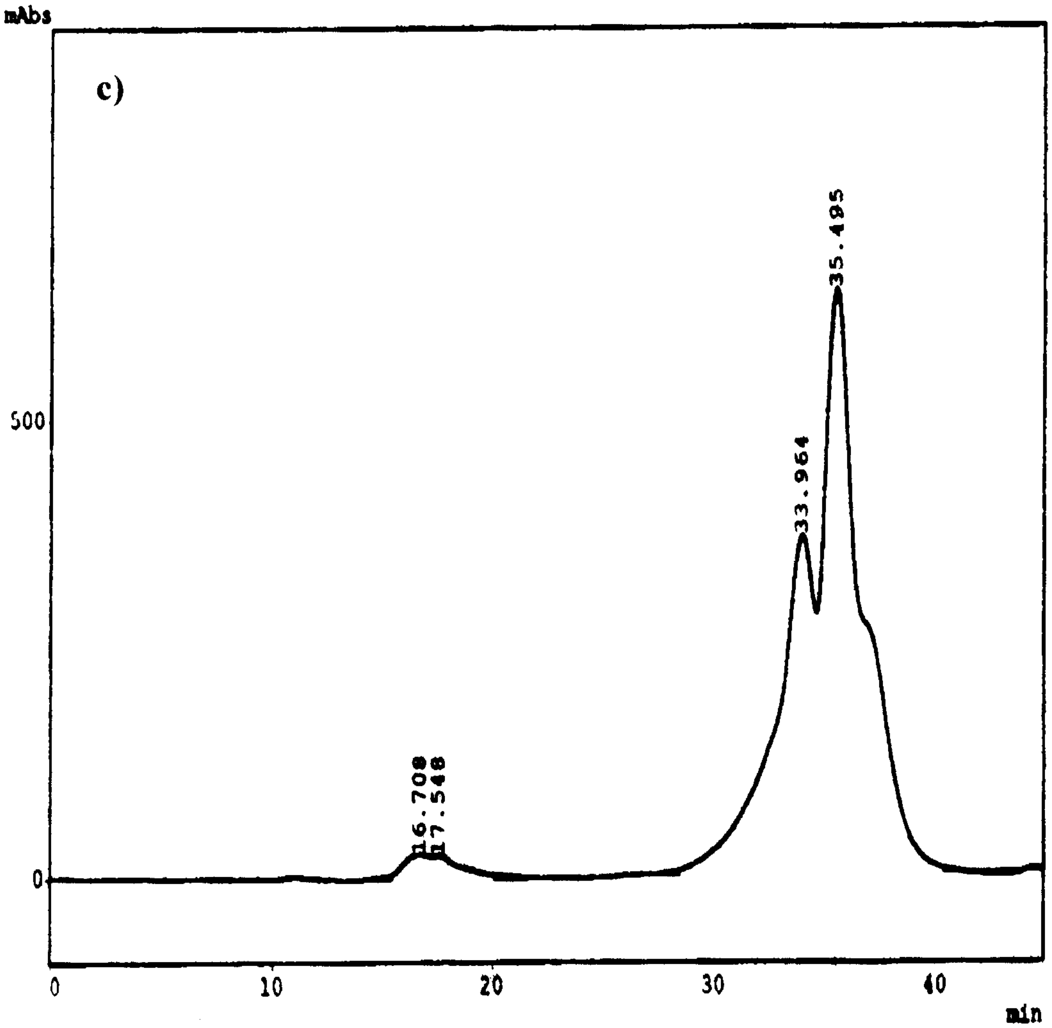

Figure 1 (*Continued from the previous page*)

grade) was purchased from Aldrich Chemical Co. (Milwaukee, WI). All other reagents used were analytical reagent grade. Monodispersed polystyrene standards were provided by Supelco (St. Louis, MO) for molecular weights ranging from 2500 to 900,000 g mol^{-1}.

Polymerization

POEA was synthesized by chemical oxidative polymerization of 0.1*M* solution of *o*-ethoxyaniline dissolved in 1*M* aqueous hydrochloric acid by dropwise addition of a chilled aqueous solution of 0.1*M* ammonium peroxydisulfate under constant stirring. The reactant molar ratio was 1 : 0.25 for *o*-ethoxyaniline and $(NH_4)_2S_2O_8$, respectively.

The temperature of the reaction was maintained at 0 ± 3°C by means of an ice-water bath. The stirring lasted 2 h to ensure completion of the reaction. The reaction mixture was then filtered, and the obtained precipitate was repeatedly washed with distilled water until it became colorless. To obtain the leached form, the produced polymer was subsequently neutralized with ammonia solution, washed with water, and dried under vacuum for 48 h.

To produce POEA with different molecular weight forms, the same procedure described above was used, except for the synthesis medium, which was controlled by adding neutral salts ($CaCl_2$ or KF) to HCl.

Molecular weight determination

Gel permeation chromatography was performed on a Shimadzu LC Model 10 AD connected to a Shimadzu UV detector SPD-10A (Shimadzu, Kyoto, Japan).

Molecular weights were determined using a 300 × 7.8-mm ID TSK gel permeation chromatography (GPC) column filled with TSK-Gel type G4000HXL supplied by TosoHaas Corp. The used mobile phase was DMF with a flow rate of 0.3 mL/min.

The standard solutions were prepared by dissolving 5 mg of the polystyrene standards in 10 mL of DMF

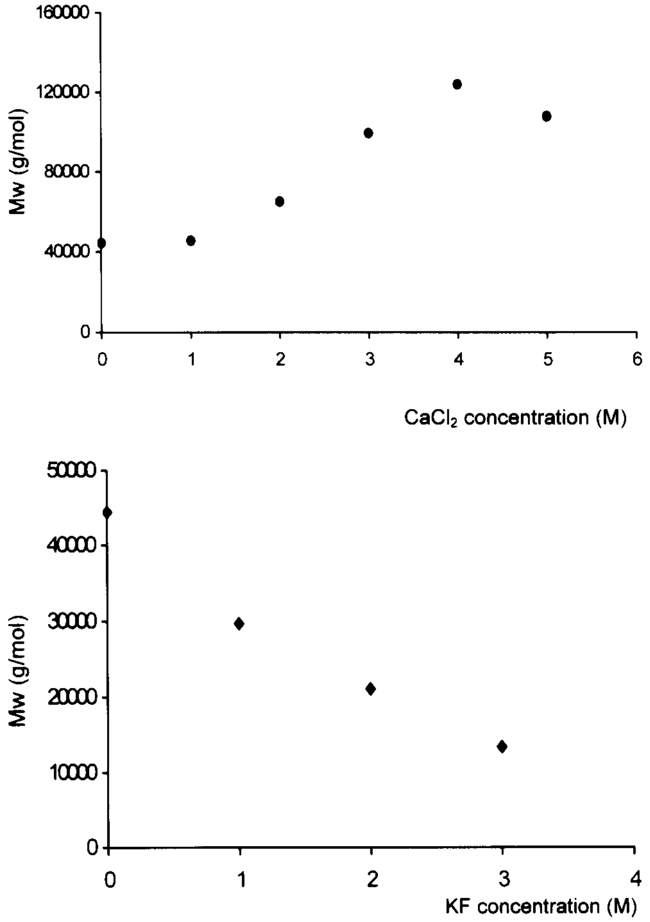

Figure 2 Molecular weight of POEA as function of (a) the $CaCl_2$ concentration and (b) the KF concentration.

and the mixture was then stirred for about 30 min. The sample solutions were prepared exactly in the same way but stirring lasted 16 h. Both standard and sample solutions were filtered through a 0.5-μm micropore syringe before injection. Sample solutions of 20 μL were injected for each experiment. The observed wavelengths were 263 nm for polystyrenes and 310 nm for POEA. The peak molecular weight (GPC molecular weight) of the polymer was obtained from the comparison of the polymer retention time with that of the polystyrene calibration curve.

Spectroscopic studies

The FTIR spectra of the alcohol-soluble and -insoluble forms of the polymer in its HCl-doped state were recorded on a Perkin–Elmer Model Paragon 1000 PC spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) in the form of a KBr pellet (compressed powder). Their electronic spectra in the doped and leached forms were obtained as a dilute solution in dimethyl sulfoxide (DMSO) using a Perkin–Elmer Lambda-25 spectrophotometer.

Soluble polymer as corrosion inhibitor

The testing of the alcohol-soluble portion of POEA as a corrosion inhibitor was carried out by the electrochemical techniques following the logarithmic polarization technique (LPT), linear polarization resistance (LPR), and the electrochemical impedance spectroscopy (EIS). For these electrochemical experiments a three-electrode cell with 0.78 cm^2 of mild steel containing 0.005% P, 0.25% Si, 1.28% Mn, 0.29% C, 0.008% S, 0.06% Cr, 0.02% Ni, 0.01% Mo, 0.03% Cu, and the rest iron, was used as a working electrode (WE), a saturated calomel electrode (SCE) as the reference electrode, and graphite as the counter electrode. Before use, the surface of mild steel was mechanically polished with wet SIC paper (grade 400–600), rinsed with distilled water, degreased in ethanol, and dried at room temperature. Before initiating the electrochemical experiments for corrosion testing, the WE was allowed to reach steady state after immersion in the cell for 1 h.

For LPT and LPR measurements a potentiostat (Autolab PGSTAT20) was used. EIS measurements were carried out using Autolab PGSTAT20 and frequency response analyzer in a frequency range of 10^5–10^{-1} Hz.

RESULTS AND DISCUSSION

The polymer obtained from *ortho*-ethoxyaniline was remarkably soluble in organic solvent in both doped and undoped states, whereas unsubstituted polyaniline proved completely insoluble. The solubility of POEA is induced by the increase in torsional angle between adjacent phenyl rings. This is attributed to steric strain exerted by the bulky group at the *ortho* position, which renders the polymer chain more flexible.[7,8] Thus, the soluble fraction of the undoped POEA in ethanol and DMF is 74 and 99%, respectively.

The alcohol-soluble portion was tested for further application as a corrosion inhibitor for mild steel under acidic media. The polymer alcohol-insoluble portion was completely soluble in DMF but was not tested in terms of corrosion inhibition efficiency because, on adding the DMF solution to the aqueous acidic one, polymer precipitation occurs.

Molecular weight of POEA for alcohol-soluble and alcohol-insoluble fractions

The GPC study was carried out on the polymer base form [Fig. 1(a)] and its alcohol-insoluble [Fig. 1(b)] and alcohol-soluble fraction [Fig. 1(c)]. Their respective gel permeation chromatograms in DMF, without adding salt, exhibit more than one peak.

The molecular weight of the alcohol-insoluble fraction is higher (800,000 g mol^{-1}) than that of the alco-

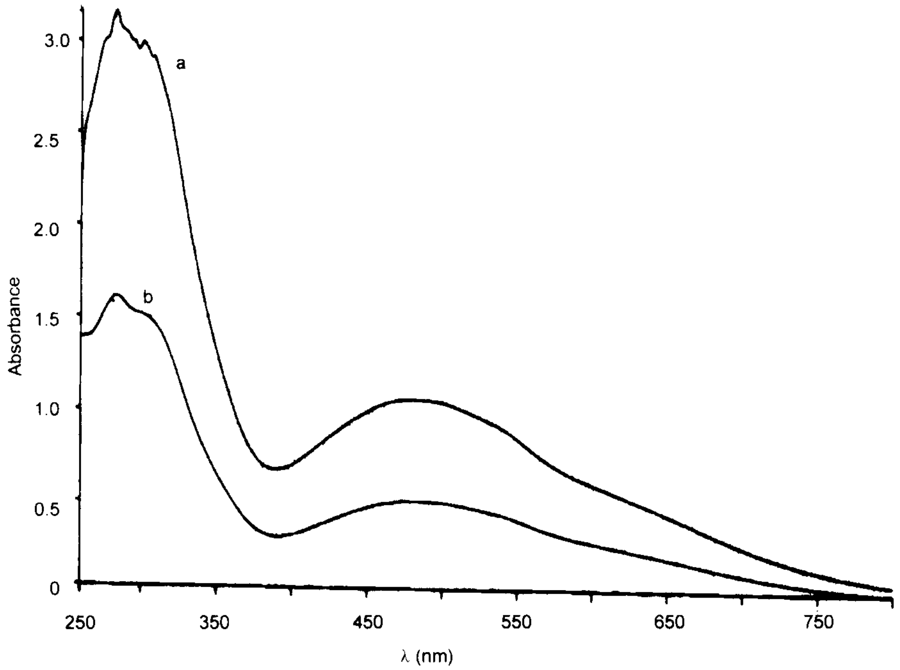

Figure 3 UV–vis solution spectra in DMSO after removing the alcohol-insoluble portion of (a) POEA-doped HCl and (b) leached POEA.

hol-soluble fraction (44,000 g mol^{-1}) and its insolubility in ethanol can be attributed to the fact that it is composed of high molecular weight fractions of POEA.

However, as reported in previous studies,[7,8] spectroscopic studies revealed that the alcohol-soluble fraction contains many more quinoid than benzoid forms, and thus has greater solubility.

Under constant polymerization conditions, the molecular weights of the resulting alcoholic form of POEA were significantly affected by the concentration of $CaCl_2$ within the electrolyte [Fig. 2(a)]. Increasing $CaCl_2$ concentration from 0 to 4*M* led to a tremendous increase in M_w from 44,000 to 124,000 g mol^{-1}. This is attributed, in fact, to the mechanism proposed for the salt effect on M_w of chemically synthesized polyaniline.[9,10]

It is well known that the rate of reaction between positively charged ions is increased by the presence of a dissolved neutral salt.[11] Hence, it is expected that the rate of reaction of radical cations with positively charged oligomers or positively charged growing polymer chains will be increased in the presence of dissolved salts.

However, regardless of the above effect, it is expected that the reaction rate with the polymer will be greater than that with the oligomer, given that the higher the molecular weight, the greater the positive charge delocalization, thus facilitating preferential reaction of the radical cation with the growing positively charged polymer chain.

On the other hand, using different concentrations of KF as a neutral salt greatly affected the molecular weights of the resulting alcoholic form of POEA [Fig. 2(b)]. In fact, increasing KF concentration from 0 to 3*M* led to a decrease in M_w from 44,000 to 13,000 g mol^{-1}.

Such a decrease in POEA molecular weight can be explained by the fact that in solutions of high ionic strength, the rate of reaction between ions of opposite charge is much lower.[11] Consequently, the rate of the controlling step (initiation) will be decreased by dissolved salt, whereas the rate of reaction between radical cations in solution or between radical cations in solution and the solid polymer will be increased.

UV–visible spectra

A DMSO solution of the HCl-doped alcohol-soluble form of POEA exhibits absorption bands at 281, 302, 452, and 503 nm [Fig. 3(a)]. However, on removal of the dopant, the absorption bands appear at 281, 304, and 491 nm [Fig. 3(b)]. The band at 503 nm in HCl-doped POEA shows that the polymer is composed of more quinoid structures compared to the alcohol-insoluble form of POEA. This observation was further validated by IR spectral studies. A similar observation holds true for the overoxidation of polyaniline[12] (PANI) attributed to the formation of pernigraniline with an absorption band at 530 nm.

A DMSO solution of HCl-doped polymer (after complete removal of alcohol-soluble portions) has a

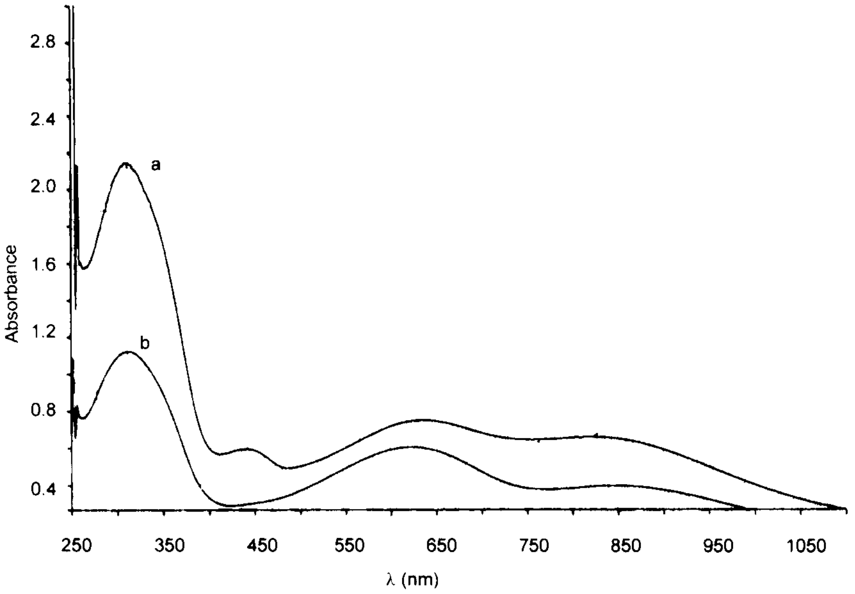

Figure 4 UV–vis solution spectra in DMSO after removing the alcohol-soluble portion of (a) POEA-doped HCl and (b) leached POEA.

green color with absorption bands at 311 (π– π^* transition), 440, and 823 nm; these are attributed to the optical absorption of the metallic polaron bands of the conducting form [Fig. 4(a)]. The hypsochromic shift of π– π^* transition and the bathochromic shift of the polaron band transition compared to those of PANI[13] illustrates the decreased conjugation caused by the *ortho*-ethoxy group. However, on removal of the dopant, the polymer solution (blue in color) exhibits absorption bands at 311 and 623 nm [Fig. 4(b)].

IR spectra

The FTIR absorption spectra in KBr for the alcohol-soluble and -insoluble forms of the polymer in its HCl-doped state are given in Figures 5 and 6, respectively.

The main difference in the IR spectra of the alcohol-soluble and -insoluble forms is the absence of the absorption band at 1499 cm^{-1} attributed to nitrogen benzoid in the alcohol-soluble form of the polymer.

In the alcohol-insoluble form of the polymer, the bands for N—B—N at 1583 and 1499 cm^{-1} are char-

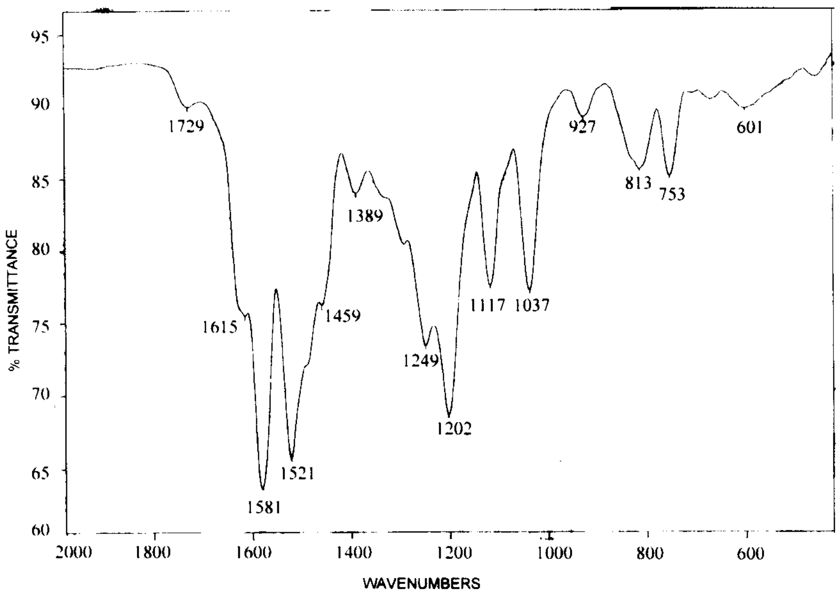

Figure 5 FTIR spectra of alcohol-soluble form of HCl-doped POEA in KBr.

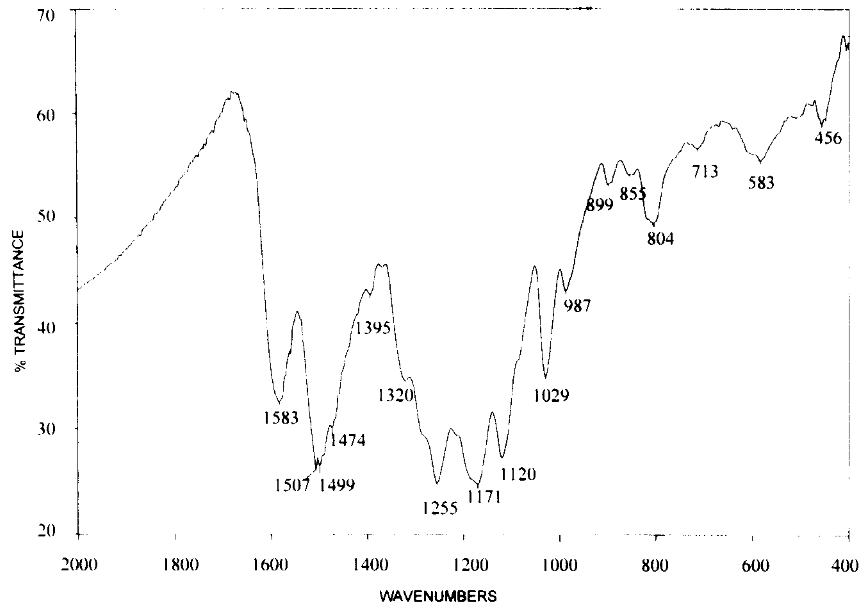

Figure 6 FTIR spectra of alcohol-insoluble form of HCl-doped POEA in KBr.

acteristic of nitrogen quinoid and benzoid (BQB), where B denotes the benzoid ring and Q denotes the quinoid ring; the presence of such bands is attributed to the conducting state of the polymer.

Evaluation of alcohol-soluble POEA as corrosion inhibitor: effect of the molecular weight on the corrosion inhibition efficiency

To investigate the effect of molecular weight of the alcohol-soluble form of POEA on the corrosion inhibition efficiencies of mild steel in acidic media, various electrochemical techniques were used such as EIS, LPR, and LPT.

The corrosion inhibition efficiency (IE) results at 100 ppm of alcohol-soluble polymer at different molecular weights are given in Table I.

Based on Table I results, it may be clearly observed that for molecular weights ranging from 13,000 to 124,000 g mol^{-1} of the POEA alcoholic form, there is no significant change in terms of inhibition efficiency. This might relate either to the fact that the adsorbed molecular population per surface unit has not been subjected to important variations (and thus no effect on the repulsive lateral interactions between neighboring molecules) or to important variations on steric effects (thus hindering the adsorption process).

TABLE I
Corrosion Inhibition Efficiency (IE) of Alcohol-Soluble POEA for Carbon Steel in 1.0*M* HCl

			LPT data			LPR data		EIS data	
Inhibitor	M_w (g mol^{-1})	Concentration (ppm)	E_{corr} (mV/SCE)	i_{corr} (μA/cm^2)	IE (%)	R_p (ohm.cm^2)	IE (%)	R_c (ohm.cm^2)	IE (%)
Without inhibitor			−483	809		27		20	
o-Ethoxyaniline	137.18	1000	−493	688	15	32	16	26	23
		10000	−491	307	62	94	71	81	75
		20000	−492	129	84	263	90	137	85
POEA (0*M* CaCl$_2$)	44385	100	−484	176	78	141	81	145	86
POEA (1*M* CaCl$_2$)	45537	100	−491	232	71	112	76	105	81
POEA (2*M* CaCl$_2$)	64949	100	−491	325	60	96	72	76	74
POEA (3*M* CaCl$_2$)	99333	100	−496	225	72	138	80	118	83
POEA (4*M* CaCl$_2$)	123821	100	−498	171	79	162	83	153	87
POEA (5*M* CaCl$_2$)	107866	100	−505	235	71	119	77	117	83
POEA (1*M* KF)	29675	100	−474	146	82	137	80	174	89
POEA (2*M* KF)	21041	100	−487	176	78	211	87	266	92
POEA (3*M* KF)	13339	100	−524	109	87	270	90	244	92

TABLE II
Influence of Temperature on the Electrochemical Parameters of Mild Steel Electrode Immersed in 1*M* HCl

Temperature (°C)	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} (μA/cm^2)
25	−483	114	96	809
35	−478	129	99	1380
45	−481	175	104	2054
60	−477	175	122	4405

Indeed, small molecular sizes have exhibited interesting efficiencies. Some attempts have been made to synthesize POEA with molecular weights lower than 13,000 g mol^{-1} while increasing KF concentration to 3*M*, but the obtained polymerization yield was extremely low because of the high viscosity of the synthesis environment induced by increased KF concentration ($C_{\text{KF}} > 3M$).

The alcohol-soluble polymer exhibits an average of 80% efficiency even with 100 ppm with no further significant improvement over a wider range of M_w (13,000 to 124,000 g mol^{-1}), whereas the *o*-phenetidine monomer presents approximately the same efficiency (85%) at 20,000 ppm. These results are evidence that the polymeric form is much better with maximum adsorption on metallic surfaces. On the other hand, the inhibition efficiencies exhibited by monomers are fairly low because of van der Waal repulsion between neighboring monomeric units, thus leaving the surface mostly unprotected.

Effect of temperature

Temperature can modify the interaction between the steel and the acidic media both without and with inhibitor. The corrosion kinetic parameters and the IE for mild steel in 1*M* HCl in the absence and the presence of 100 ppm of the alcoholic form of POEA (M_w = 13,000 g mol^{-1}) in the temperature range 25–60°C are given in Tables II and III. The current corrosion density increased with increasing temperature both in uninhibited and inhibited solutions, and the values of inhibition efficiency of the alcohol form of POEA are almost constant in the temperature range studied. Arrhenius plots for the corrosion current density of mild steel are given in Figure 7. The activation energies can be calculated using the following relationships:

$$I_{\text{corr}} = K \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

$$I'_{\text{corr}} = K \exp\left(-\frac{E'_a}{RT}\right) \tag{2}$$

where E_a and *EInfa* are the apparent activation corrosion energies in the absence and the presence of the inhibitor, respectively; and *K* is a constant. The calculated values of E_a and E'_a are 39 and 12 kJ mol^{-1}, respectively. The reduced activation energy in the presence of the alcoholic form of POEA may be attributed to the chemisorption of the POEA inhibitor on the steel surface and the corrosion process corresponds to a different mechanism of steel dissolution in the presence of the inhibitor.

Adsorption isotherm

The mechanism of the corrosion inhibition of mild steel in 1*M* HCl of the alcoholic form of POEA proceeds by a simple adsorption model (Fig.8). If this assumption is valid, the apparent corrosion rate of the inhibited steel electrode is proportional to the surface area not covered by POEA, and the fraction of the surface covered by adsorbed molecules of POEA is referred to as θ. The degree of coverage θ of the metal

TABLE III
Influence of Temperature on the Electrochemical Parameters of Mild Steel Electrode Immersed in 1*M* HCl + 100 ppm of the Alcoholic Form of POEA (M_w = 13,000 g mol^{-1})

Temperature (°C)	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} (μA/cm^2)	*E* (%)
25	−524	150	133	109	87
35	−505	123	121	124	91
45	−507	128	90	155	92
60	−527	141	99	180	96

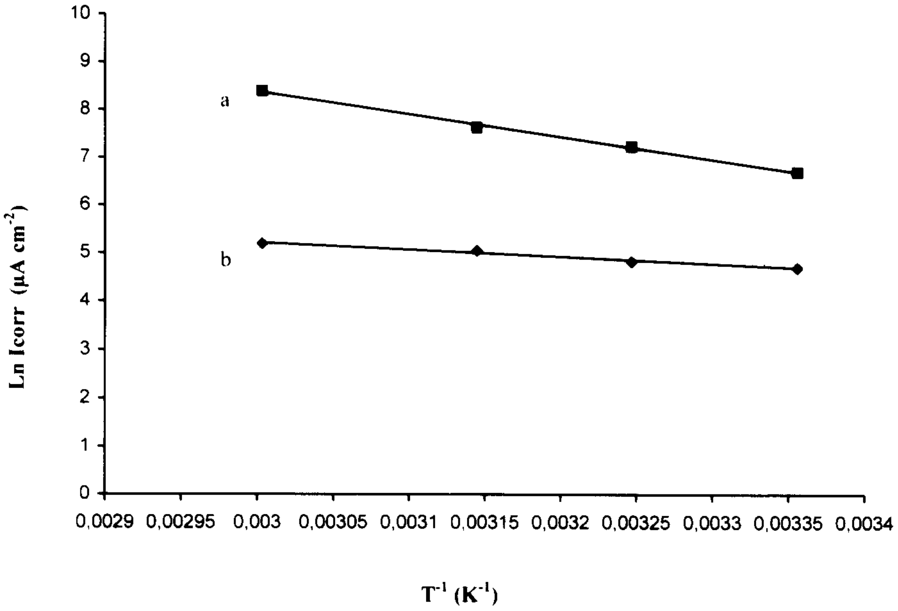

Figure 7 Arrhenius slopes calculated from corrosion current density for mild steel in: (a) 1*M* HCl and (b) 1*M* HCl + 100 ppm of the alcoholic form of POEA (M_w = 13,000 g mol^{-1}).

surface by an adsorbed inhibitor was calculated using the following equations:

$$\theta = 1 - \frac{i}{i_0} \tag{3}$$

where i_0 and i are the corrosion rates in the absence and the presence of inhibitor measured by the LPT method, respectively.

$$\theta = 1 - \frac{R_{p0}}{R_p} \tag{4}$$

where R_{p0} and R_p are the polarization resistance in the absence and the presence of inhibitor measured by the LPR method, respectively.

$$\theta = 1 - \frac{Cd_i}{Cd_0} \tag{5}$$

where Cd_0 and Cd_i are the double-layer capacitance in the absence and the presence of inhibitor measured by the EIS method, respectively.

Using the obtained θ values (Table IV) within a computer program for a regression analysis, it was

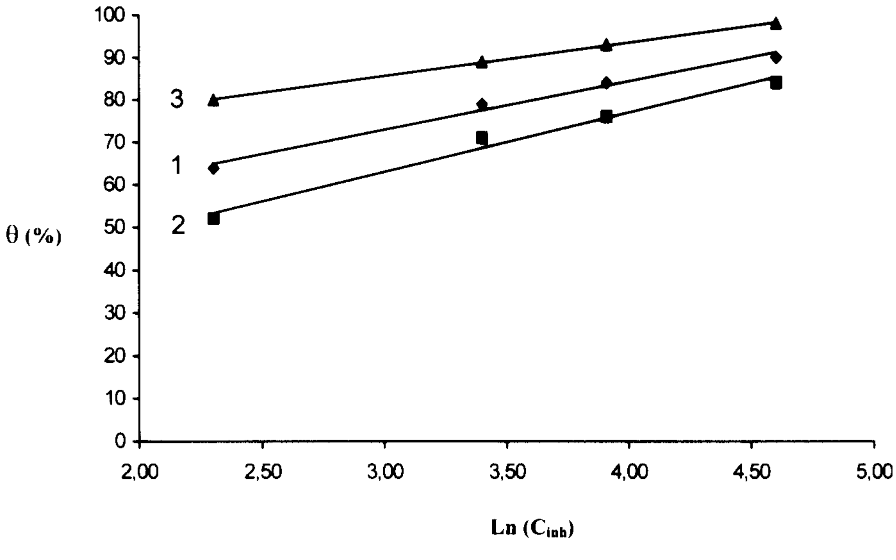

Figure 8 Temkin isotherm adsorption model of the alcoholic form of POEA on the mild steel in 1*M* HCl from: (1) LPR data, (2) LPT data, and (3) EIS data.

TABLE IV
Degree of Surface Coverage (θ) of Mild Steel in 1M HCl Containing Different Concentrations of the Alcoholic Form of POEA (M_w = 13,000 g mol^{-1}) Determined by LPT Method, LPR Method, 2nd EIS Method

	LPT method				LPR method		EIS method			
Conc. (ppm)	E_{corr} (mV/SCE)	l_{corr} (μA/cm^2)	b_a (mV/dec)	b_c (mV/dec)	θ (%)	R_p ($\Omega \cdot$ cm^2)	θ (%)	R_{et} ($\Omega \cdot cm^2$)	C_{dl} (μF/cm^2)	θ (%)
Blank	−483	809	114	96	—	27	—	20	369	—
10	−504	386	101	137	52	74	64	73	72	80
30	−504	235	121	127	71	130	79	101	40	89
50	−512	197	101	136	76	165	84	137	24	93
100	−524	109	150	133	87	270	90	244	9	98

found that the adsorption of the alcoholic form of POEA on mild steel is described by the adsorption of Temkin isotherm. Straight lines with coefficients of correlation in the range 0.9861–0.9990, were obtained by use of the LPT, LPR, and EIS methods.

The applicability of Temkin adsorption isotherm confirms the assumption of a monolayer adsorption on an energetically uniform, heterogeneous metal surface with interactions in the adsorption layer.

CONCLUSIONS

Considering the above obtained results, it can be concluded that the present study has clearly demonstrated the possibility of producing both high and low molecular weight POEA by chemical polymerization by adding controlled amounts of neutral salts to the electrolyte medium. The salt effect on the molecular weight of POEA can be explained by charge-screening effects.

The polymerization of *o*-ethoxyaniline yields two types of polymers, which are soluble in DMSO and DMF, whereas 74% of the polymer is soluble in ethanol. This solubility in ethanol is attributed not only to the quinoid forms within the polymer but to the low molecular weight of this fraction as well.

The molecular weight of the inhibitor under investigation in its polymeric form did not affect the inhibition efficiency. However, it can be stated that the polymeric form exhibits higher efficiencies compared to those of the monomeric form. This is attributed to the decrease in the van der Waal repulsion between neighboring molecules.

The presence of the alcoholic form of POEA in hydrochloric acid solution decreases the apparent activation corrosion energy value and reinforces the suggestion concerning the chemisorptive character of the adsorption. The adsorption of the inhibitor under investigation is described by the Temkin adsorption isotherm.

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