Effects of Reaction Conditions on the Formation of Poly(2-Vinylpyridine) Coatings by Electropolymerization

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The effects of reaction conditions on the formation of poly(2-vinylpyridine) coatings on mild steel by electropolymerization have been investigated. Over the ranges studied, the relative effects of these reaction conditions on the weight of the coating produced is found to decrease as follows: monomer concentration > solution pH > methanol concentration > solution temperature. The optimum conditions for coating formation are to use a solution with a composition of 0.25 M 2-vinylpyridine, 15 vol% methanol, and pH 5.0 at a temperature of 20°C. If the monomer concentration is too high, the coating formed is soft and tacky; if it is too low, a thin and non-uniform coating is produced. Methanol concentrations between 15 and 25 vol% are required to produce uniform and thick films. Coating weights decrease at electropolymerization temperatures above 40°C, presumably due to an increase in polymer solubility. The polymer films become thicker and more uniform as electrolysis continues up to two hours. Ammonium perchlorate is found to be the most suitable electrolyte for the process, although its actual concentration has little impact on film quality.

INTRODUCTION

Coatings of polyvinylpyridines and their copolymers, as well as their metallic complexes, are of interest due to their good conductivity, high corrosion resistance, electrocatalytic capability, low cost, and simplicity of manufacture.[1-11] Sekine et al.[12] found that poly(2-vinylpyridine) coatings which formed on mild steel by electropolymerization provided superior corrosion protection. On the other hand, de Bruyne et al.[13] were unable to form poly(2-vinylpyridine) films on mild steel, although they were successful when zinc substrates were used. Ling et al.[14] found that the solution pH plays a critical role in forming poly(2-vinylpyridine) coatings by electropolymerization. When the pH is adjusted close to the *p*Ka value of the monomer, free-radical electropolymerization can occur, leading to good quality films on a variety of metals, including mild steel. Recently, the mechanism of the process was studied by surface enhanced Raman scattering spectroscopy and cyclic voltammetry on polymer-modified electrodes.[15] The results suggested a mechanism involving protonation of the monomer in the aqueous solution and adsorption of the protonated monomer on the cathodic surface, followed by its reduction to generate free radicals, initiation, and propagation of polymer chains, and frequently occurring termination by uptake of hydrogen radicals (*Figure* 1). Another important part of the proposed mechanism is the protonation and reaction of newly formed polymer chains to form crosslinked and branched polymer coatings.

Two electrochemical techniques that have been used to carry out electropolymerization of 2-vinylpyridine are chronoamperometry and cyclic potential sweep (CPS) electrolysis. Both techniques employ a three-electrode configuration consisting of a working electrode, counter electrode, and reference electrode. An electronic feedback circuit in the potentiostat simultaneously allows the working electrode potential to be controlled with respect to that of the reference electrode and the current flowing between the working electrode and counter electrode to be measured. In chronoamperometry, the potential of the working electrode is maintained constant, and the resulting current is monitored over time. The CPS method is an extension of chronoamperometry that

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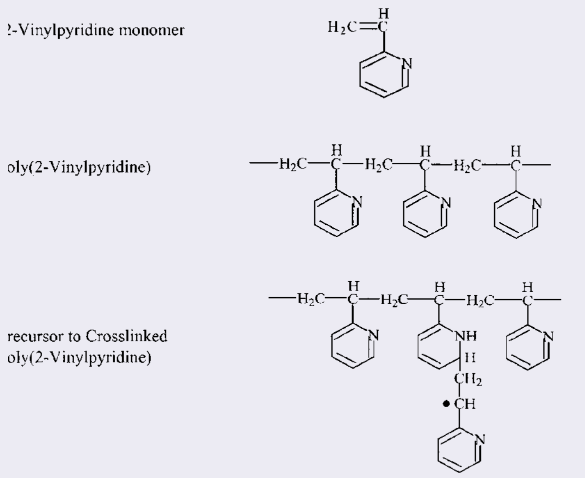


Figure 1—Chemical structure of 2-vinylpyridine monomer, poly(2-vinylpyridine) and crosslinked poly(2-vinylpyridine).

applies cyclic voltammetry to control the electrolysis. The working electrode potential is varied at a constant rate between fixed limits, first in one direction and then in the opposite direction. Electrolysis is carried out by the repeated application of this scan cycle and the resulting current is monitored over time. Of the various electrochemical techniques investigated for forming the polymer coatings, the CPS technique produced the best films since it is most compatible with the various steps involved in the electropolymerization process[16]. This technique involves the repeated application of triangular linear sweeps of the electrode potential, similar to what is done in cyclic voltammetry.

In this paper, the effects of reaction conditions including monomer and methanol concentrations, solution temperature, and duration of electrolysis on the formation of poly(2-vinylpyridine) coatings on mild steel by electropolymerization are reported. The investigation was carried out via the CPS and chronoamperometric techniques. The relative importance of these parameters has also been determined through experiments using an orthogonal-fractional-factorial design.

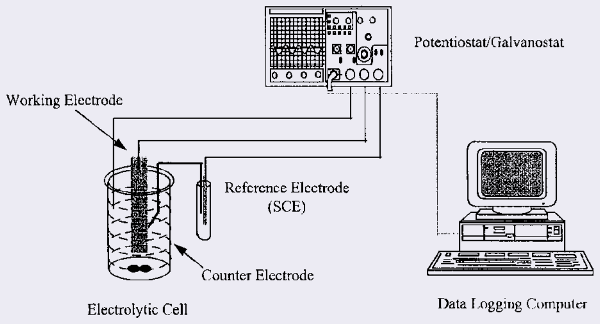


Figure 2—Experimental apparatus for in situ electropolymerization of poly(2-vinylpyridine) coatings on mild steel substrates from aqueous solutions.

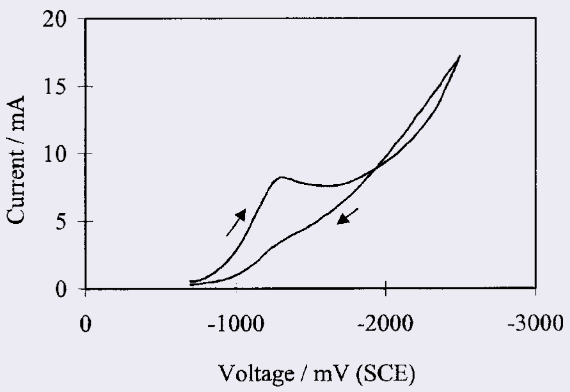


Figure 3—Typical cyclic voltammogram obtained during the electropolymerization of 2-vinylpyridine at 20°C. Electrolyte is composed of an aqueous solution containing 0.05 M NH_4ClO_4, 0.25 M 2-vinylpyridine, and 10 vol% methanol at pH 4.8. Voltammetric scan rate = 30 mV/s.

EXPERIMENTAL

2-Vinylpyridine (Aldrich Chemical Co.) was purified to remove the inhibitor (0.1 wt% *p-tert*-butylcatechol) by distillation at 70°C under vacuum (97.8 kPa Hg). All other chemicals were analytical grade and used without further purification. Electropolymerization was carried out in aqueous solutions containing 2-vinylpyridine monomer, methanol, an inorganic electrolyte, and its corresponding acid to adjust the pH to 4.8. The inorganic electrolytes considered in this study included NH_4ClO_4, $KClO_4$, $HClO_4$, NH_4Cl, KCl, $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_3PO_4$, and H_3PO_4. The purpose of adding methanol was to ensure complete dissolution of the monomer in the solution. The procedure for preparing these solutions was to dissolve sufficient monomer in an aqueous methanol solution to make up the desired concentration and then add the appropriate electrolyte and acid. All solutions were prepared with ultra-pure water (Millipore® ultra-pure water system) and a total volume of 60 ml solution was used in each experiment.

A standard three-electrode system comprised of working, counter, and reference electrodes was used to carry out the electrochemical experiments (*Figure* 2). The working electrode was a mild steel coupon (SAE 1018-1020) with an active surface area of 5.5 cm^2 placed in the center of the electrochemical cell, surrounded by a platinum coil counter electrode wound along the internal wall of the cell. The reference electrode was a saturated calomel electrode (SCE, Aldrich Chemical Co.) and the potentials reported in this work correspond to the working electrode potential measured on the SCE scale.

The working electrode was cleaned ultrasonically first in a soap solution for 30 min and then polished with SiC-type abrasive paper (up to 1200 grade). Degreasing was carried out with trichloroethylene for two minutes, followed by washing with soap solution to remove the grease and trichloroethylene, rinsing with a large amount of deionized water, and finally rinsing with ultra-pure water. The prepared metal samples were stored in a desiccator until needed. The platinum counter electrode was cleaned by immersion in Electrode-Cleaner® solution (supplied by Fisher Scientific and containing 500 mL 2-(iso)-propanol, 500 mL ethyl ether, 250 mL concentrated HCl, and 250 mL H_2O) for two minutes and then rinsed with tap water and finally ultra-pure water.

A potentiostat (EG&G 273) was used to conduct cyclic voltammetry and chronoamperometry experiments. The output from the experiments was recorded on a data-logging computer (JPC 386SX) and was monitored online on the computer screen. The solution was continuously agitated with a magnetic stir bar throughout the electrolysis. The solution temperature was maintained by placing the cell in a water bath during the electrolysis. Electrolysis was carried out using two techniques: chronoamperometry at a constant working electrode potential of –1.3 V and CPS electrolysis over the working electrode potential range of –0.7 to –2.5 V at 30 mV/s.

A typical response obtained during a forward and backward scan of cyclic voltammetry is shown in *Figure* 3. This response shows the variation of the cathodic current due to electropolymerization as the electrode potential is first varied from –0.7 V to –2.5 V and then from –2.5 V back to –0.7 V. To monitor possible changes in electrode reactions or mechanisms, it is often useful to determine the half-wave potential ($E_{1/2}$) of a current plateau or peak (potential at which the current reaches half of its maximum value). The $E_{1/2}$ value for any particular reaction does not vary with changes in concentration of any reactants or products and so serves as a "fingerprint" for the reaction. In our analysis, we monitored the $E_{1/2}$ value associated with the peak appearing in the forward scan (*Figure* 3).

Since the potential is scanned at a linear rate during CPS electrolysis, an equivalent way to present the electrode response is to plot the current as a function of time. This would leave the response during the forward scan of *Figure* 3, for example, unchanged but cause the response during the backward scan to appear as a mirror image of what appears in *Figure* 3, reflected about a vertical line at the point of potential reversal. Presentation of the response on a current-time scale is much more convenient when electrolysis is carried out repeatedly over many cycles for extended periods of time, as in the case of CPS electrolysis.

After electrolysis, the coated samples were rinsed with deionized water and dried in vacuum (29 in.Hg) at room temperature for one day. Thermal curing was performed optionally at 120~130°C for 30 min. Attempts to measure the average molecular weight of the polymer coatings using methods such as gel permeation chromatography met with little success since it was not possible to dissolve them completely in organic solvents. This was likely due to the considerable amount of crosslinking occurring during electropolymerization of 2-vinylpyridine.[15]

Once the polymer coatings were formed, they were examined using confocal scanning laser microscopy (CSLM). Confocal microscopy is an optical method that differs from conventional techniques in that only light from the focal plane is reflected back to the detector. This eliminates any interference from above and below the focal plane that occurs in conventional optical microscopy and leads to less distortion. The use of a laser source allows the incident beam to focus on a tiny spot on the sample and gives CSLM excellent lateral resolution. Although this technique has been extensively applied in the biological field, we demonstrated that it can be successfully used to image polymer coatings in a previous article on the electropolymerization of 2-vinylpyridine.[17]

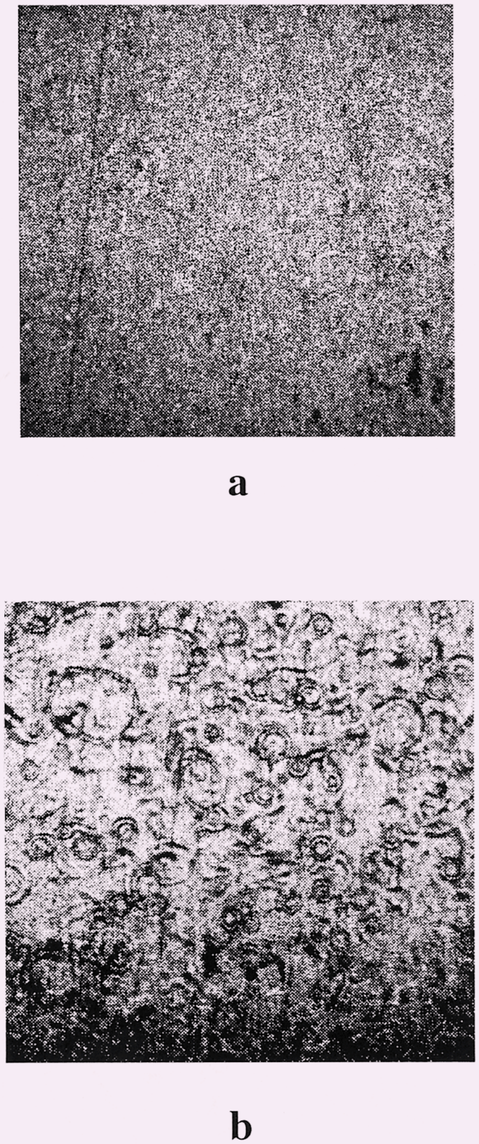


Figure 4—CSLM images of electropolymerized poly(2-vinylpyridine) coatings: (a) 1mm x 1mm area of a coating obtained after two hours of CPS electrolysis between –0.7 and –2.5 V at a scan rate of 30 mV/s; and (b) 4 mm x 4mm area of a coating obtained after two hours of chronoamperometric electrolysis at –1.3 V. In both cases, the electrolyte composition is the same as that shown in Figure 3.

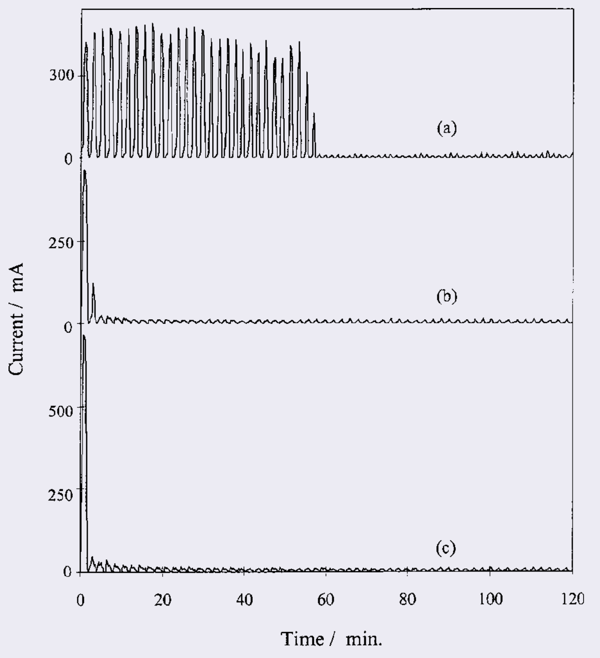


Figure 5—I-t diagrams of cyclic potential sweep electrolysis (between –0.7 and –2.5 V at 30 mV/s) of poly(2-vinylpyridine) coatings on mild steel at 20°C and (a) 0.1 M, (b) 0.25 M, and (c) 0.35 M 2-vinylpyridine. Solution composition: pH 4.8, 20 vol% methanol, and 0.05 M NH_4ClO_4.

A particularly useful property of poly(2-vinylpyridine) in this regard is that its coatings are partially translucent to visible light. This permits CSLM not only to produce an image of the top surface of the coating but also to scan through its interior and generate an image of its lower surface at the polymer/metal interface. From this information, it becomes possible to measure the film thickness directly at individual points along the coating surface as well as to obtain three-dimensional images of the coating.

Figure 4 shows examples of two CSLM images of electropolymerized 2-vinylpyridine coatings. These examples have been chosen to show that CSLM can provide good detail of the coatings. A high quality coating that is smooth and uniform is shown in *Figure* 4a. This should be contrasted with the image in *Figure* 4b of an uneven and irregular coating on which craters formed by the evolution of H_2 gas bubbles during electropolymerization are clearly evident.

RESULTS AND DISCUSSIONS

Effect of Monomer Concentration

The results of experiments studying the effect of monomer concentration are summarized in *Table* 1 and some corresponding current–time (I–t) diagrams are shown in *Figure* 5. It is found that the half-wave potential ($E_{1/2}$) for 2-vinylpyridine reduction remains virtually constant at –1.0 V regardless of the concentration of monomer, as would be expected. When the monomer concentration is too low (<0.15 M), intense evolution of hydrogen is observed at the cathode surface and only thin and non-uniform coatings formed. Presumably, there is not enough monomer at the electrode surface to compete with hydrogen for adsorption on the electrode surface. Since the solution is already being well stirred mechanically, the evolution of gas bubbles makes little or no additional contribution to mass transfer of the monomer. As the monomer concentration increases, the coverage of the electrode surface by the monomer increases and the polymerization rate increases and thicker and more uniform films are formed. However, when the monomer concentration becomes too high (exceeding 0.3 M), coating quality suffers. For one thing, it becomes difficult to dissolve all of the monomer in the electrolyte. Also, a high monomer concentration may lead to a high rate of initiation relative to that of propagation, resulting in a polymer coating with lower molecular weight and higher solubility in the electrolyte. These effects would lead to a softer, tackier and more uneven coating as is, in fact, observed.

The I–t diagrams of the CPS processes (*Figure* 5) support these explanations. The electrode responses show the higher frequency oscillations characteristic of current flow within each cycle that are superimposed on a longer-term current envelope. As recently shown,[16] the formation of a thick and uniform coating tends to be associated with an electrode response that shows a sharp drop in the longer term current envelope soon after the onset of electrolysis. This is due to the formation of a passive polymer film on the electrode surface. Such a reduction in current has been observed in the previous studies on the electropolymerization of 2-vinylpyridine[12-14,16] and agrees with the expected behavior for the formation of a passive film. These results are consistent with those reported by Rafique et al.[9] who found poly(2-vinylpyridine) to have an electrical conductivity of 7.9×10^{-12} S/m. (It should be noted that the incorporation of transition metals into the polymer increases its conductivity dramatically.) When the coating is poor or slowly forming, the decline in current is more gradual. At low monomer concentration (e.g., 0.1 M), the electrolysis current does

Table 1—Effect of 2-Vinylpyridine Monomer Concentration on Poly(2-Vinylpyridine) Film Formation on Mild Steel after Two Hours of Cyclic Potential Sweep Electrolysis at 20°C

2-Vinylpyridine Concentration (M)	Coating Weight (mg/cm^2)	Comment
0.10	0.22	Extremely thin film; intense H_2 evolution
0.15	0.40	Thin, but uniform film; intense H_2 evolution
0.20	0.58	Thick and uniform film
0.25	0.62	Thick and uniform film
0.30	2.05	Thick, but non-uniform and tacky film
0.35	2.51	Unevenly distributed film which appeared to flow over the electrode surface

Solution composition: pH 4.8, 20 vol % methanol, 0.05 M NH_4ClO_4.

not decrease for the first hour (*Figure* 5a), reflecting that little polymer forms on the electrode surface. At higher monomer concentrations (e.g., 0.25 and 0.35 M), the initial current is higher but the subsequent drop is more abrupt (*Figures* 5b and 5c), indicating rapid formation of polymer films on the electrode surfaces due to rapid electropolymerization. However, this does not always correspond to a good quality coating. As discussed previously, a non-uniform and soft coating formed at very high (e.g., 0.35 M) monomer concentration.

At this point, it should also be noted that the color of the coatings formed by electropolymerization under all conditions reported in this paper is yellowy-brown rather than colorless as is the case for the same polymer formed by bulk methods. This agrees with what has been consistently found by those who have investigated the electropolymerization of 2-vinylpyridine.[12-15] Similar findings have been observed by others during the electropolymerization of other polymer coatings.[18] As discussed previously,[15] this coloring is likely attributable to the fact that electrolysis produces a much more branched and crosslinked polymer structure than do bulk methods.

Effect of Methanol Concentration

The effects of the concentration of methanol in the solution on coating formation are summarized in *Table* 2 and some corresponding I–t diagrams are shown in *Figure* 6. The effect of low methanol concentration (e.g., 1 to 5 vol%) is similar to that of very high monomer concentration. The solubility of the monomer in the solvent is not high enough to make a solution with the desired monomer concentration (e.g., 0.25 M) without adding $HClO_4$ to increase the extent of monomer protonation and form 2-vinylpyridinium ions which are soluble in water. This low methanol concentration also causes the polymer to have a relatively low solubility and to rapidly form a coating on the electrode surface which, as shown in *Figure* 6c, leads to the rapid drop in current soon after the onset of electrolysis. Unfortunately, a non-uniform and soft coating forms as the result of this rapid film formation process. As the methanol concentration increases (>10 vol%), the polymer becomes more soluble in the solvent, and a harder and more uniform coating forms on the electrode surface. The current still drops quickly after the onset of the electrolysis (*Figure* 6b). However, when the methanol concentration reaches above 30 vol%, hydrogen evolution becomes more intense during the electrolysis, especially at the beginning of the process. The I-t diagram (*Figure* 6a) shows that in the first 30 to 40 min there is no current drop, indicating that whatever coating is present during this period is not capable of suppressing hydrogen evolution. However, a close look at the detailed electrode response during each cycle shows that electroreduction of the monomer still occurs during this period. This suggests that the reduction product may be dissolving in the solution soon after its formation. This is likely due to the fact that the high methanol content in the solvent leads to a high solubility toward not only the monomer, but also the primary radicals and the polymer product. The film formed, although thinner, is uniform.

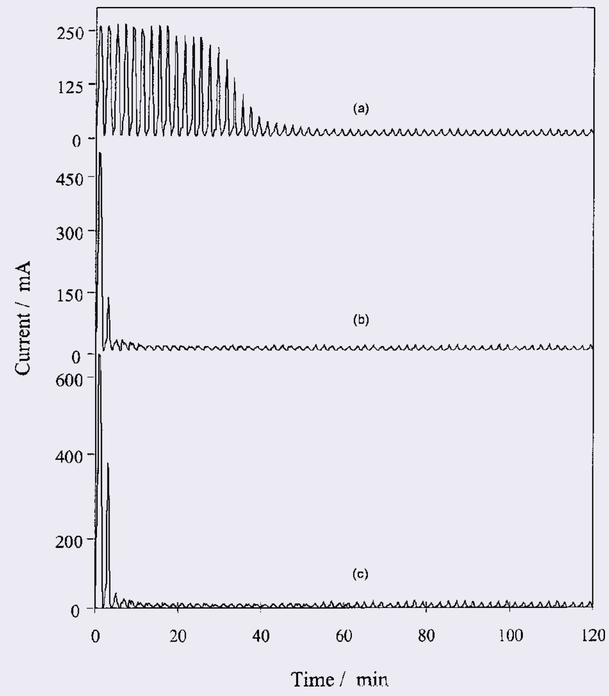


Figure 6—I-t diagrams of cyclic potential sweep electrolysis (between –0.7 and –2.5 V at 30 mV/s) of poly(2-vinylpyridine) coatings on mild steel at 20°C and (a) 40, (b) 20, and (c) 5 vol% methanol. Solution composition: pH 4.8, 0.25 M 2-vinylpyridine, 0.05 M NH_4ClO_4.

Effect of Temperature

The effects of the temperature of the solution on the formation of coatings are relatively mild (*Table* 3). When the temperature is below 40°C, thick and uniform coatings are obtained in two hours. When the temperature exceeds 40°C, the coating weight begins to decrease as the temperature rises. This may be due to the fact that more polymer product dissolves in the electrolyte at

Table 2—Effect of Methanol Concentration on Poly(2-Vinylpyridine) Film Formation on Mild Steel after Two Hours of Cyclic Potential Sweep Electrolysis at 20°C

Methanol Concentration (vol.%)	Coating Weight (mg/cm²)	Comment
1	0.53	Very thin and non-uniform film
5	0.75	Thin and non-uniform film
10	1.18	Thin, but uniform film
15	1.55	Thick and uniform film
20	1.44	Thick and uniform film
25	1.16	Thick and uniform film
30	0.87	Thin, but uniform, film
40	0.42	Thin, but uniform, film

Solution composition: pH 4.8, 0.25 M 2-vinylpyridine, 0.05 M NH_4ClO_4.

Table 3—Effect of Solution Temperature on Poly(2-Vinylpyridine) Film Formation on Mild Steel after Two Hours of Cyclic Potential Sweep Electrolysis

Operating Temperature (°C)	Coating Weight (mg/cm^2)	Comment
10	1.49	Thick and uniform film; light yellow electrolyte
20	1.44	Thick and uniform film; yellow electrolyte
30	1.49	Thick and uniform film; yellow electrolyte
40	1.55	Thick and uniform film; yellow electrolyte
50	1.33	Uniform film; deeper yellow electrolyte
60	1.18	Very uniform film; deeper yellow electrolyte
70	1.13	Very uniform film; very dark yellow electrolyte

Solution composition: pH 4.8, 0.25 M 2-vinylpyridine, 20 vol % methanol, 0.05 M NH_4ClO_4.

Table 4—Effect of Electrolysis Duration on Poly(2-Vinylpyridine) Film Formation on Mild Steel after Two Hours of Cyclic Potential Sweep Electrolysis at 20°C

Electrolysis Duration (min)	Coating Weight (mg/cm^2)	Comment
20	0.40	Thin and unevenly distributed film
30	0.71	Thin and not very uniform film
60	0.91	Thicker and more uniform film
90	1.27	Uniform film
120	1.44	Thick and uniform film
180	1.36	Thick and uniform film
270	1.25	Thick and uniform film
300	1.27	Thick and uniform film
600	1.24	Thick and uniform film

Solution composition: pH 4.8, 0.25 M 2-vinylpyridine, 20 vol % methanol, 0.05 M NH_4ClO_4.

higher temperature or that termination occurs more readily. The higher polymer solubility could be caused by an increase in the rate of initiation relative to that of chain propagation, leading to a higher radical concentration and the formation of shorter, lower molecular weight polymer chains. Another possible contributing factor would be an increase in the rate of termination relative to that of propagation. The CPS I–t diagrams (*Figure* 7) provide more information on the processes that occur. At the highest temperature (e.g., 70°C), the electrolysis current throughout the whole process is relatively high (*Figure* 7c), suggesting that the rate of electropolymerization is high. At lower temperatures (e.g., 40° and 10°C), the current is much lower (*Figure* 7a). Nevertheless, the initial current at any temperature drops rapidly after the onset of the electrolysis, indicating the formation of protective coatings in all cases. It is also important to mention that at a high temperature much less hydrogen evolution is observed on the cathode surface, although the current is higher than at the lower temperature. The explanation for this effect is not well understood yet.

Another effect that is particularly evident as temperature is varied is the change in color of the electrolyte. As temperature is raised, the electrolyte turns a darker yellow color during electrolysis. Moreover, the change in color occurs more rapidly. Such observations have been noted previously by others studying electropolymerization of 2-vinylpyridine[12-14] and other monomers.[18] In fact, this behavior is not unique to electropolymerization and has been observed previously in bulk polymerization of this and other vinyl monomers by other researchers[19-22] who showed that it arose due to the presence of low molecular weight polymers or oligomers in solution. Our present findings are consistent with this earlier work and lend further support to the idea that coatings with shorter, lower molecular weight and more soluble polymer chains are being formed as the temperature is increased.

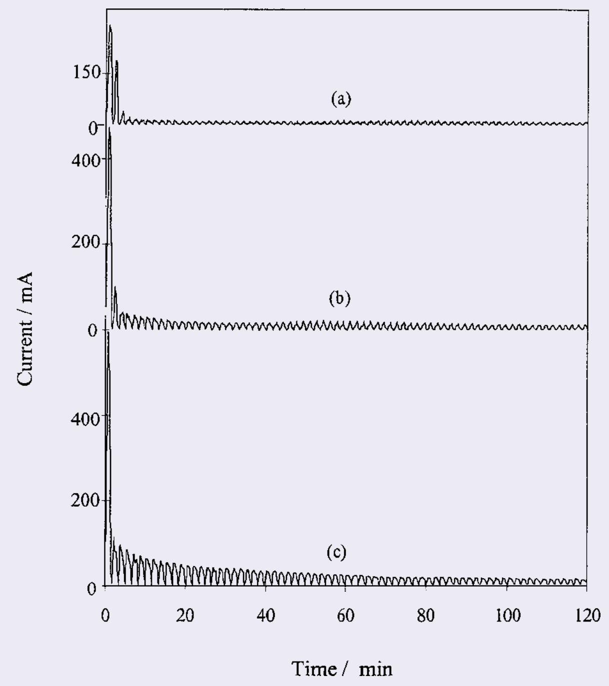


Figure 7—I-t diagrams of cyclic potential sweep electrolysis (between –0.7 and –2.5 V at 30 mV/s) of poly(2-vinylpyridine) coatings on mild steel at (a) 10°C, (b) 40°C, and (c) 70°C. Solution composition: pH 4.8, 0.25 M 2-vinylpyridine, 20 vol% methanol, 0.05 M NH_4ClO_4.

Effect of Duration of Electrolysis

The effects of the duration of electrolysis on the electropolymerization process have been studied for time periods between 15 min and 10 hr (*Table* 4). Although a polymer deposit can be observed after the first cycle of the potential sweep (i.e., in two minutes), it is thin and non-uniform. Further electrolysis not only increases the thickness of the coating, but also makes it more uniform. This is likely directly related to the self-healing nature of the electropolymerization technique. At the beginning of the process, the electrode surface is fresh and the

Table 5—Effects of Various Electrolytes on Poly(2-Vinylpyridine) Film Formation on Mild Steel after Two Hours of Chronoamperometric Electrolysis at–1.3 V (SCE) and 20°C

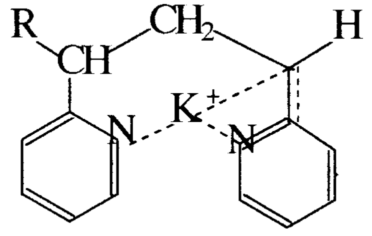
Electrolyte	H_2 Evolution	Coating Weight (mg/cm²)	Comment
NH_4ClO_4	visible	0.95	Thick, uniform and glassy film
$KClO_4$	visible	0.78	Uniform and glassy film
$HClO_4$	visible	1.04	Thick, uniform and glassy film
NH_4Cl	not visible	0.40	Thin and uniform, but powdery film
KCl	not visible	0.33	Thin and uniform, but powdery film
$(NH_4)_2SO_4$	not visible	0.65	Uniform, but powdery film
NH_4NO_3	not visible	0.56	Uniform, but powdery film
$(NH_4)_3PO_4$	not visible	0.64	Uniform, but powdery film

Solution Composition: pH 4.8, 0.25 M 2-vinylpyridine, 20 vol % methanol.

electrolysis occurs over a large surface area. The current is high, resulting in a considerable amount of initiation in a short period. Meanwhile, hydrogen evolution is intense at the fresh electrode surface, which interferes greatly with film formation and causes the polymer film to be unevenly distributed. Once the electrode surface becomes covered with the polymer film (although it may still be thin and uneven), hydrogen evolution is greatly suppressed. During the remaining cycles, coating formation occurs preferentially on the more thinly coated areas that have lower resistance. Consequently, the film becomes more uniform in thickness as it grows. At the same time, the rate of electropolymerization decreases and the coating reaches a limiting thickness.

Effect of Added Electrolyte

Various inorganic compounds, such as NH_4ClO_4, $KClO_4$, KCl, NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_3PO_4$, and H_3PO_4, have been tested as added electrolytes for the process. The acid corresponding to each anion was used to adjust the solution pH to 4.8. The voltammograms obtained using different electrolytes are quite similar. The $E_{1/2}$ of 2-vinylpyridine reduction in the different electrolytes shifts only slightly. Coating formation was carried out by chronoamperometric electrolysis at –1.3 V for two hours and the results are summarized in *Table* 5. The results show clearly that the nature of the anion has a strong effect on the electropolymerization. The addition of an electrolyte containing perchlorate leads to thicker, harder, more adherent and more uniform coatings than those obtained in chloride-, sulfate-, or phosphate-based solutions. Comparison of the coatings obtained in the different perchlorate solutions indicates that the nature of the cation has a smaller effect than that of the anion, with somewhat thinner films being produced in $KClO_4$- $HClO_4$ solutions than in NH_4ClO_4-$HClO_4$ and $HClO_4$ alone (note that $HClO_4$ was added to adjust pH). A possible explanation for this behavior comes from previous observations[23] of the strong intramolecular interaction between alkali metal ions and the pyridine rings of the terminal and penultimate units of poly(2-vinylpyridine) chains, as shown in the following:



One would therefore expect it to be more difficult to dissociate an alkali metal cation from the polymer chain than NH_4^+. Previous work on this monomer and others[15,18] has indicated that polymer chains formed during electropolymerization may themselves undergo further electron transfer so that crosslinking and branching occur. In the case of poly(2-vinylpyridine), this could involve protonation and subsequent electroreduction of the pyridine rings to form radical sites. Since this process would require the displacement of the pre-existing cation by the H^+ ion, electropolymerization would occur to a smaller extent in the presence of $KClO_4$ than NH_4ClO_4, as observed in our results in *Table* 5.

When NH_4Cl is used as the electrolyte with HCl to adjust the solution pH, the coating is loose and powdery, although no hydrogen bubbles appear on the electrode surface during the electrolysis. Similar to the previous situation with the perchlorate anions, an even thinner film is obtained with KCl as the added electrolyte than with NH_4Cl. When $(NH_4)_2SO_4$, NH_4NO_3, or $(NH_4)_3PO_4$ is used as the electrolyte with H_2SO_4, HNO_3, or H_3PO_4 to adjust the solution pH, respectively, loose and powdery films similar to those obtained with chloride electrolytes are obtained. No hydrogen evolution is observed during these experiments.

The role of the anions observed here during electropolymerization of poly(2-vinylpyridine) is related to the effect of anions reported previously on the spin and drop coating of poly(4-vinylpyridine)-based films on electrodes. Oh and Faulkner showed from fluores-

Table 6—Effect of NH_4ClO_4 Concentration on Poly(2-Vinylpyridine) Film Formation on Mild Steel after Two Hours of Cyclic Potential Sweep Electrolysis at 20°C

NH_4ClO_4 Concentration (M)	Specific Conductivity (S/m)	Coating Weight (mg/cm²)
0.01	0.9715	1.58
0.05	1.4735	1.44
0.1	2.0079	1.44
0.2	2.3145	1.16
0.35	3.1435	1.24
0.5	4.0954	1.29

Solution composition: pH 4.8, 0.25 M 2-vinylpyridine, 20 vol% methanol.

Table 7—Important Operating Parameters and Their Three-Level Ranges Studied

Opeating Parameter Levels	(A) Solution Temperature (°C)	(B) 2-Vinylpyridine Concentration (M)	(C) Methanol Concentration (vol%)	(D) Solution pH
I	20	0.15	5	4.5
II	30	0.25	15	5.0
III	40	0.35	25	5.5

cence emission and IR spectra and from conductivity and chronocoulometry experiments that coatings formed in the presence of perchlorate were also completely dehydrated and impermeable with a compact and rigid structure.[24,25] They attributed these effects to the influence of ClO_4^- on both water and polymer structure. As shown previously by Walrafen,[26] ClO_4^- does not form directed hydrogen bonds with water and can cause an extensive breakdown of the hydrogen-bonded water structure. Since electroneutrality requires that ClO_4^- ions remain in the polymer films, water will be driven out of the polymer phase. Furthermore, ClO_4^- has been shown to form direct bonds with the polymer which would be expected to cause a significant amount of crosslinking between polymer segments.[27,28]

The observation that the best coatings obtained in our study are produced in the presence of ClO_4^- suggests that the optimum conditions for electropolymerization of poly(2-vinylpyridine) are those that lead to a coating with a dehydrated, compact and rigid structure. The ability of ClO_4^- to promote a crosslinked polymer structure is consistent with a number of our previous findings[14,15] indicating that a considerable amount of branching and/or crosslinking occurs during electropolymerization. The role of the anion on the polymer structure described previously is also consistent with another of our observations[14] that, of those studied, the coatings formed in the presence of ClO_4^- provided the highest corrosion resistance for the underlying mild steel. One would expect a dry, compact, and crosslinked layer to be the most impermeable and protective. Another factor that may contribute to the poor quality of coatings in chloride solutions is the strong interaction that can occur between Cl^- and the metal electrode itself and their ability to form surface compounds.[29] In this way, Cl^- ions would interfere with electropolymerization and H_2 evolution.

It is interesting to note that the evolution of hydrogen gas is observed in the presence of perchlorate electrolytes, but not in the presence of the others tested. This indicates that H_2 evolution is not necessarily detrimental to coating formation.

The NH_4ClO_4 concentration has also been varied to test its effect on the electropolymerization process (*Table* 6). Although the specific conductivity of the electrolytes varies by a factor of 4 with the change in NH_4ClO_4 concentration, the half-wave potential for 2-vinylpyridine reduction is found to be virtually unaffected and the coatings formed are similar in their uniformity and thickness.

Statistical Study of the Effect of the Reaction Conditions

To investigate the relative importance of the reaction conditions to coating weight and their optimum combination for the process, standard four-parameter and three-level orthogonal-fractional-factorial designed experiments[30,31] were carried out. The parameters studied, their range, the detailed experimental design, and the experimental results are given in *Tables* 7 and 8. The statistical analysis (i.e., the calculation of the orthogonal-fractional-factorial averages and the maximum differences of the averages) was used to determine the relative importance of the parameters on coating weight over the ranges studied. These results were then combined with qualitative assessment of coating uniformity to obtain the overall optimum conditions (*Table* 9). The relative importance of the parameters to the electropolymerization process over the ranges studied is found to be factor B (2-vinylpyridine concentration), factor D (solution pH), factor C (methanol concentration), and factor A (temperature).

It is also found that, $\overline{A_I}$, $\overline{A_{II}}$ and $\overline{A_{III}}$ are relatively close in value, indicating that a change in operating temperature over the range of 20° to 40°C has little impact on the process. Although $\overline{A_{III}}$ (40°C) appears to the best solution temperature, $\overline{A_I}$ (20°C) is recommended due to its convenience in operating the process and to the fact that the temperature is not a strongly acting variable of the process. $\overline{B_I}$ (0.15 M of monomer) corresponds to the thinnest film in the entire series of experiments and, therefore, the use of a low monomer concentration should be avoided. On the other hand, although high monomer concentration increases the film thickness the most, it

Table 8—Standard Four-Parameter and Three-Level Orthogonal-Fractional-Factorial Design and the Experimental Results[a]

Test No.	(A) Solution Temperature	(B) 2-Vinylpyridine Concentration	(C) Methanol Concentration	(D) Solution pH	Coating Weight (mg/cm²)	Comment
1	I	I	I	I	0.29	Extremely thin and uniform film
2	I	II	II	II	1.96	Thick and uniform film
3	I	III	III	III	1.16	Uniform film
4	II	I	II	III	0.29	Extremely thin and uniform film
5	II	II	III	I	1.11	Uniform film
6	II	III	I	II	3.36	Thick, but non-uniform, soft and tacky film
7	III	I	III	II	0.67	Thin but uniform film
8	III	II	I	III	1.67	Thick and uniform film
9	III	III	II	I	2.98	Thick, but non-uniform, soft and tacky film

(a) The values of the different levels of each parameter are given in *Table* 7.

Table 9—Results of Statistical Analysis: the Fractional-Factorial Averages and their Maximum Differences

Fractional-Factorial Averages	$\overline{A_I}$	$\overline{A_{II}}$	$\overline{A_{III}}$	$\overline{B_I}$	$\overline{B_{II}}$	$\overline{B_{III}}$	$\overline{C_I}$	$\overline{C_{II}}$	$\overline{C_{III}}$	$\overline{D_I}$	$\overline{D_{II}}$	$\overline{D_{III}}$
	6.27	8.73	9.77	2.30	8.70	13.77	9.77	9.60	5.40	8.03	11.00	5.73
Maximum Differences		R_A			R_B			R_C			R_D	
		3.50			11.74			4.34			5.27	

leads to non-uniform and soft films. Consequently, an intermediate concentration of 0.25 M $\left(\overline{B_{II}}\right)$ is suggested as the optimum level for the monomer concentration. $\overline{C_I}$ and $\overline{C_{II}}$ are close to each other and much higher than $\overline{C_{III}}$, indicating that the suitable methanol content should be between 5 and 15%. Considering the difficulty of dissolving the monomer in the aqueous medium, $\overline{C_{II}}$ (15 vol%) is recommended. In the narrow range of pH 4.5 to 5.5, factor D (solution pH) shows that the best result is obtained at a solution pH of 5 $\left(\overline{D_{II}}\right)$ which is closest to the *p*Ka value of 2-vinylpyridine.[32] Any pH value away from the *p*Ka value leads to thinner coatings. These results are consistent with our previously reported findings.[14] Thus, on the basis of this analysis, the optimum operating conditions for the process are $\overline{A_I}$, $\overline{B_{II}}$, $\overline{C_{II}}$, and $\overline{D_{II}}$, i.e., a solution at 20°C with pH 5.0 containing 0.25 M 2-vinylpyridine and 15 vol% methanol.

CONCLUSIONS

The effects of reaction conditions on the formation of poly(2-vinylpyridine) coatings on mild steel by electropolymerization have been investigated. While high monomer concentration is found to favor the formation of thick and uniform coatings, an excessive amount of monomer (>0.25 M) results in soft and tacky films. Low methanol concentration (<10 vol%) in the solution makes monomer dissolution in the electrolyte difficult and leads to thin and patchy polymer films. Although high methanol concentration (>25 vol%) increases the solubility of the monomer in the solution, it also increases polymer solubility and leads to a uniform but thin film. High operating temperature results in the formation of a thick and uniform coating although the polymer film likely has a low average molecular weight. Although the polymerization rate is low at low temperatures such as 10°C, this also leads to a thick and uniform film, which may be directly related to a higher average molecular weight of the product. For the first two hours of electrolysis, the thickness of the polymer films increases with time. After the first two hours, the duration of electrolysis does not have any additional effect on film thickness and uniformity. Of the various inorganic compounds tested as electrolytes, NH_4ClO_4 is found to be most suitable for poly(2-vinylpyridine) film formation by electropolymerization, although its actual concentration has little effect on the process. The use of other anions in the electrolyte often leads to loose and powdery coatings. Orthogonal-fractional-factorial design analysis has also been used to evaluate the relative importance of various parameters on the weight of the resulting polymer films. It was found that over the range studied, the relative importance of the parameters was 2-vinylpyridine concentration, solution pH, methanol concentration and solution temperature. The analysis also indicates that a 2-vinylpyridine concentration of 0.25 M, an electrolyte pH of 5, a methanol concentration of 15 vol% and a solution temperature of 20°C provide the optimum conditions over the range tested in this study.

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