A Mechanism for Electropolymerization of 2-Vinylpyridine Coatings on Metal Surfaces

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ABSTRACT: The mechanism of coating formation by electropolymerization of poly(2-vinylpyridine) has been studied on a copper electrode by surface-enhanced Raman scattering spectroscopy and cyclic voltammetry. The experimental results are consistent with a mechanism in which 2-vinylpyridine molecules become protonated in acidic aqueous solutions and are selectively adsorbed on cathodic surfaces. The adsorbed 2-vinylpyridinium ions then undergo electrochemical reduction to free radicals, which initiate polymerization by combining with neutral 2-vinylpyridine molecules also present in solution. The pH of the electrolyte has been found to be critical for this process. On the basis of the voltammetric experiments, an additional mechanism for polymer growth on the cathodic surface at more negative potentials is proposed. This involves protonation of nitrogen sites along the newly formed poly(2-vinylpyridine) chains, followed by their reduction to form polymeric radicals that can initiate chain branching. In this way, inactive polymer chains can be reactivated and highly branched and cross-linked poly(2-vinylpyridine) coatings can be formed, leading to the relatively low solubility of these coatings in typical organic solvents.

Introduction

Electropolymerization of vinylpyridines has attracted considerable attention due to important applications in modified electrodes,[1−4] microelectronic transistors,[5,6] matrixes for incorporating electroactive groups at electrode surfaces,[7,8] polyelectrolytes,[9,10] and corrosion inhibitors.[11−13] Most of the research so far, however, has focused on these new materials and the measurement of their polymer and coating properties.[14−20] Little research has been carried out to study the mechanisms of coating formation by electropolymerization. This lack of understanding of the mechanisms may have contributed to poor-quality coatings and poor reproducibility.[2,12,21]

In investigating the mechanism of coating formation by electropolymerization, the techniques of cyclic voltammetry (CV), and surface-enhanced Raman scattering (SERS) spectroscopy have been used. CV, in which the electrode potential is scanned and the current response is recorded, is a technique that has been used both to investigate reaction mechanisms and to carry out the electropolymerization. It not only can provide dynamic and kinetic information on the system of interest but also may be applied directly to perform the electrolysis, using so-called potential sweep or scanned potential electrolysis.[1,22−24] Its special features for studying electropolymerization have been summarized by Funt.[4]

In SERS, a laser beam is used to analyze the material adsorbed on a metal surface. The technique has been found to be particularly valuable in studying adsorption at electrode/solution interfaces.[25−27] Most of these SERS studies, however, deal with either macromolecular or micromolecular adsorption on metal surfaces under static conditions, rather than with the dynamic in situ polymerization of the monomeric molecules at the metal surfaces.

In this work, a study of the mechanism of poly(2-vinylpyridine) coating formation on copper electrode surfaces by electropolymerization of the monomer has been carried out. The extent of protonation of the 2-vinylpyridine molecule in aqueous solutions is examined as a function of pH by ordinary Raman spectroscopy. The adsorption of neutral and protonated 2-vinylpyridine molecules is investigated over a wide range of pH and applied electrode potentials by SERS. The process of electropolymerization of 2-vinylpyridine on the copper electrode surface has been monitored in situ with SERS. The electron-transfer processes occurring at the cathode in 2-vinylpyridine electropolymerization are studied using CV. On the basis of the results of these experiments and previous work done in our laboratory, a mechanism of poly(2-vinylpyridine) coating formation by electropolymerization of the monomer is proposed. Although we have reported the electropolymerization onto mild steel in our previous studies,[13,28] copper electrodes are used in the SERS experiments since they produce an enhanced Raman spectrum.[25] Furthermore, we have found from our other studies that the effectiveness of the electropolymerization of 2-vinylpyridine does not depend on the nature of the substrates, so the SERS results should also be applicable to electropolymerization on mild steel. Similar behavior has been observed in the electropolymerization of phenol on metal substrates.[29,30]

Experimental Section

Reagents. 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). All other chemicals were analytical grade and used without further purification. All electrolytes used in this study were aqueous and contained 0.05 M NH_4ClO_4 and 20 vol % methanol in addition to 2-vinylpyridine monomer or poly(2-vinylpyridine). Controlled amounts of $HClO_4$ or NH_4OH were added to the electrolyte to adjust the pH as required. All electrolytes were prepared with ultrapure water (Millipore ultrapure water system).

Electrodes. A three-electrode system comprised of a 3-mm copper (>99.99) disk working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode

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(SCE, Aldrich Chemical Co.) was used in the experiments. Potentials reported in this work are all on the SCE scale. The working and counter electrodes were first cleaned ultrasonically in a soap solution and then degreased with trichloroethylene. They were then washed with soap solution to remove any remaining grease and trichloroethylene and rinsed with a large amount of deionized water and finally with ultrapure water. The working electrodes were then mechanically polished with SiC-type abrasive paper (up to 1500 grade). To achieve the optimum SERS spectrum, the working electrodes were roughened ex situ electrochemically by applying several oxidation−reduction cycles between −1.0 and 1.0 V at 30 mV/s in 0.1 M KCl solution.[26,31]

Experimental Techniques. The SERS and CV experiments were performed in a specially designed spectroelectrochemical cell in which the anodic and cathodic compartments were separated by a porous glass frit.[27] Also, prior to each experiment, the electrolyte was transferred to the cell and purged with N_2 for 10 min to remove any dissolved O_2. All experiments were performed at 20 °C. A potentiostat (EG&G 273) was used to conduct the electropolymerization. The output of the experiments was recorded on a data-logging computer (Wailab 486i) and monitored online on the computer screen. Raman spectra were obtained with a Ramascope 1000 (Renishaw) system. A Melles Griot He−Ne laser (17 mW, with a wavelength of 362.8 nm) equipped with a holographic notch filter was employed as the source of illumination. A computer (Pentium 167, JPC) was used to record the spectral data. The in situ Raman spectroscopic studies of 2-vinylpyridine adsorption and electropolymerization on electrode surfaces were performed simultaneously with the chronoamperometric electrolysis.

For comparative purposes, poly(2-vinylpyridine) was also formed by conventional bulk polymerization with 1 wt % benzoyl peroxide as free radical initiator at room temperature.[32] The polymer was precipitated by pouring the reaction solution into *n*-hexane. The crude polymer was then purified by dissolving in tetrahydrofuran, filtering, and precipitating again in *n*-hexane. The polymer was finally dried under vacuum at room temperature.

Results and Discussion

Ordinary Raman Spectroscopy of the Bulk Solutions. The ordinary Raman spectrum of pure 2-vinylpyridine is available from the literature.[33] Raman spectra of 0.25 M 2-vinylpyridine aqueous solutions (with 20% methanol) were obtained at pH 10.0, 7.4, 4.8, and 1.0 by adding concentrated NH_4OH or $HClO_4$ to the electrolyte (initial pH 7.4). Comparison of these spectra (Figure 1) with that of pure 2-vinylpyridine shows that the solution spectra contain the water absorbance at high wavenumber (>3100 cm^{-1}) and the methanol absorbances at 2848, 2952, and 1453 cm^{-1}. The characteristic band for ClO_4^- at 932 cm^{-1} appears in the solution spectra as well, increasing in intensity as the ClO_4^- ion concentration increases. The results indicate that no strong pyridine−chlorine association exists in the system. The ClO_4^- species in the electrolyte exists in the form of nonassociated ions.[33]

From Figure 1, the effects of solution pH on the extent of 2-vinylpyridine protonation can be seen. The most striking differences among these spectra are in the 1550−1650 cm^{-1} double-bond stretching region, which are shown in detail in Figure 2. The spectrum at low pH (Figure 2d) has a distinct band at 1619 cm^{-1}, which has been reported previously[34] and is normally assigned to the ν_{8a} ring mode of the pyridinium ion on the basis of similar bands in substituted[35] and unsubstituted [36] salts. This band becomes weaker as the solution pH

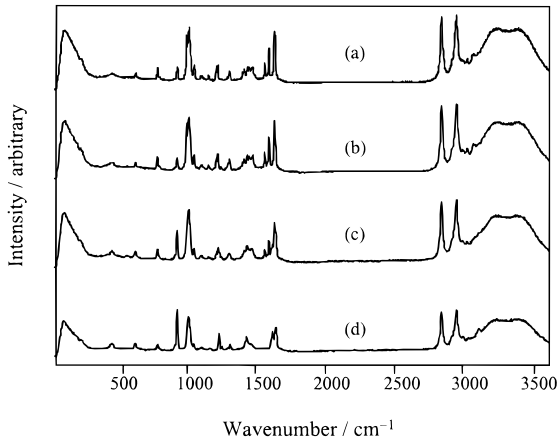


Figure 1. Ordinary Raman spectra of 0.25 M 2-vinylpyridine aqueous solution (with 20% methanol) at different solution pH, adjusted with concentrated $HClO_4$ or NH_4OH: (a) pH 10.0, (b) pH 7.4, (c) pH 4.8, (d) pH 1.0.

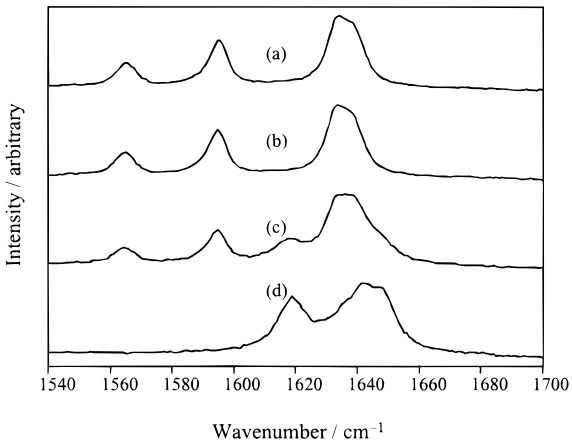


Figure 2. Detailed Raman spectra (1540−1700 cm^{-1}) from 0.25 M 2-vinylpyridine aqueous solution: (a) pH 10.0, (b) pH 7, (c) pH 4.8, (d) pH 1.0.

increases to 4.8 (Figure 2c) and totally vanishes at pH 7.4 (Figure 2b) and 10 (Figure 2a). Bands at 1565 and 1595 cm^{-1} are observed from spectra of electrolytes of pH 7.4 and 10.0. These bands are normally assigned to the ν_{8a} and ν_{8b} modes of the neutral pyridine ring.[33] These bands diminish as solution pH decreases (Figure 2c) and vanish at very low pH (Figure 2d). Comparison of parts a and b of Figure 2 shows that the spectra above pH 7.4 are identical. This indicates that the protonation of 2-vinylpyridine is no longer decreasing and that 2-vinylpyridine is likely completely unprotonated once pH 7.4 is reached.

These spectra confirm the pH dependence of 2-vinylpyridine protonation in aqueous solution and the role of pH in electropolymerization that had been postulated earlier.[13] At high pH (e.g., pH >7.4), most of the 2-vinylpyridine molecules exist in their unprotonated form, and a further increase in pH has no effect on 2-vinylpyridine protonation. At low solution pH (e.g., pH 1), most of the 2-vinylpyridine molecules exist in their protonated form. When the solution pH has an intermediate value (e.g., pH 4.8), both neutral and protonated 2-vinylpyridine species coexist in the solution, and consequently, the corresponding spectrum has the characteristics of both forms. These results are also consistent with the pK_a value of 4.92 reported for the protonation of 2-vinylpyridine.[37] It is only at these intermediate values of pH when both neutral and

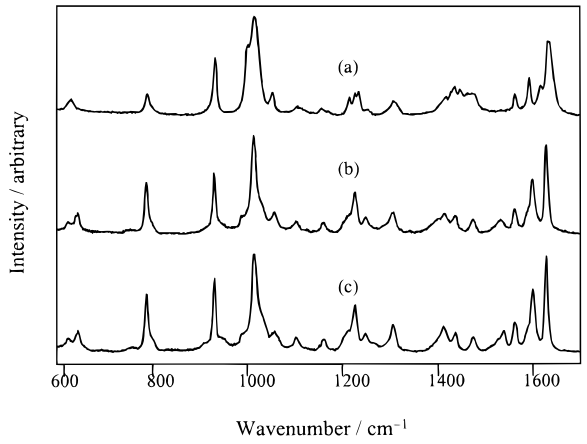


Figure 3. SERS spectra of a copper electrode surface from a solution at pH 4.8 containing 0.25 M 2-vinylpyridine: (a) at open circuit potential ($E_{opc} = -0.18$ V) when no current flows, (b) working electrode at −0.1 V with anodic current flowing, (c) working electrode at 0 V with anodic current flowing.

protonated forms of 2-vinylpyridine are present that thick and uniform polymer coatings can be formed via electropolymerization.[13]

SERS at Copper Electrode Surfaces. When the electrolytic cell is operated at its open circuit potential (E_{opc}) of −0.18 V with a solution of pH 4.8, the SERS spectrum (Figure 3a) of a copper electrode immersed in a 0.25 M 2-vinylpyridine solution is similar to the ordinary Raman spectrum (Figure 1). The only significant difference is the absence of the characteristic bands of water at wavenumbers above 3100 cm^{-1} and methanol at 2848 and 2952 cm^{-1}. Other than these absences, the high wavenumber portion of the spectrum provided no new information and so was omitted from Figure 3a. The absence of the bands for water and methanol suggests that 2-vinylpyridine is preferentially adsorbed at the electrode surface. The ClO_4^- characteristic band at 932 cm^{-1} also appears in the SERS spectrum, indicating that the ClO_4^- ions are adsorbed on the electrode surface as well. When the working electrode potential (E_w) is made more positive (i.e., $E_w > E_{opc} = -0.18$ V), the characteristic band for the pyridinium ion at 1619 cm^{-1} disappears from the spectra (Figure 3b,c), while the characteristic band for the neutral pyridine ring at 1565 cm^{-1} remains. This suggests that only neutral vinylpyridine remains adsorbed on the copper surface and that pyridinium ions are repelled from the surface of the working electrode. Since the spectrum at −0.1 V is virtually identical to that at 0 V, desorption of pyridinium ions at the copper surface appears to be complete at −0.1 V and is no longer dependent on the magnitude of the anodic electrode potential.

When the potential of the working electrode is decreased below E_{opc}, the spectra in Figure 4 are obtained. The characteristic band of the pyridinium ion at 1632 cm^{-1} shows no position shift but a decrease in relative intensity as the potential decreases. The characteristic band of the pyridinium ion at 1619 cm^{-1} shifts to 1611 cm^{-1} at −0.3 V (Figure 4b), to 1608 cm^{-1} at −0.6 V (Figure 4c), and eventually to 1600 cm^{-1} at −1.0 V and below, where it overlaps with one of the fingerprint bands of the neutral pyridine ring (Figure 4d,e). The characteristic band of the neutral pyridine ring at 1565 cm^{-1} appears at all potentials, whereas the one at 1595 cm^{-1} starts to shift to a higher wavenumber soon after E_w becomes more negative than E_{opc} (Figure 4b). The

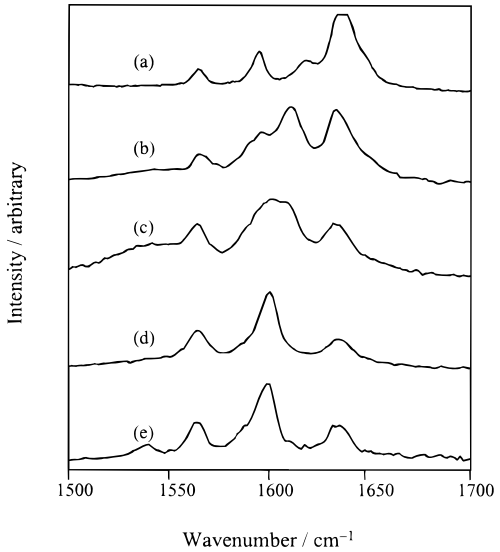
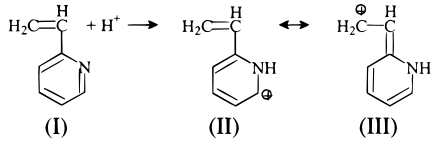


Figure 4. SERS spectra (1500−1700 cm^{-1}) of a copper electrode surface from a solution at pH 4.8 containing 0.25 M 2-vinylpyridine: (a) at open circuit potential ($E_{opc} = -0.18$ V), (b) at −0.3 V, (c) at −0.6 V, (d) at −1.0 V, (e) at −1.3 V.

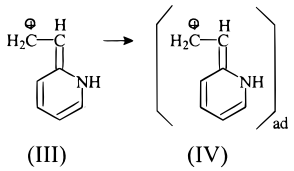
band reaches 1600 cm^{-1} and overlaps with the shifted pyridinium band at −0.6 V (Figure 4c), remaining at this wavenumber as the potential becomes more negative (Figure 4d,e). Comparison of part a of Figure 4 with parts d and e shows that the neutral form of 2-vinylpyridine becomes enriched at the working electrode relative to the 2-vinylpyridinium ion as the electrode potential becomes more negative, indicating that neutralization of the pyridinium ion is occurring as a result of electron transfer at the cathode.

In an earlier study,[13] we proposed a mechanism for the initiation and propagation steps in the electropolymerization of 2-vinylpyridine based on the results of voltammetry experiments and confocal scanning laser microscopy analysis. The Raman spectra presented in the current study support this mechanism and allow us to enlarge upon and provide more details of the proposed mechanism. A portion of the 2-vinylpyridine (I) at values of pH between 4.0 and 5.5 is protonated to form the pyridinium ion that can be represented by a variety of canonical forms (e.g., II and III):



(1)

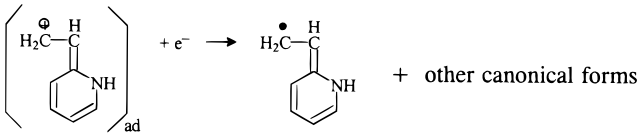
On the basis of the Raman spectra shown in this study, these ions are electrostatically attracted to and adsorb at the cathode surface upon cathodic polarization of the electrode:



(2)

The adsorbed pyridinium ions (IV) are then reduced by

electron transfer at the cathode to form neutral free radicals (V):



(3)

These free radicals (V) may then combine with the neutral 2-vinylpyridine molecules, which are also shown to be adsorbed at the cathode or which may be in the solution adjacent to the electrode to form the polymer chain via a series of steps that we have described previously.[13] Our observation in Figure 4 that the neutral form of pyridine becomes increasingly dominant over the protonated form as the electrode potential becomes more cathodic can be explained by this mechanism. As the potential becomes more negative, the electron-transfer reaction 3 is pushed further to the right, thereby decreasing the amount of pyridinium ions at the surface.

Once the electrode potential is decreased to −1.0 V and below, no further change in the SERS spectrum can be observed (Figure 4d,e). When the working electrode potential is decreased further, extensive hydrogen evolution is observed at the surface of the electrode, in addition to the reduction of 2-vinylpyridine and the formation of a polymer coating. As the working electrode potential is made more negative, the intensity of hydrogen evolution increases further. The evolution of hydrogen bubbles leads to a very noisy SERS spectrum and sometimes a disruption of the entire process.

From this analysis, it is evident that the SERS spectra are most informative regarding monomer reduction before H_2 evolution begins to occur. To investigate processes related to electropolymerization that may be occurring at more negative potentials, where H_2 evolution would normally occur, we used another approach, as described in the next section.

Cyclic Voltammetry of a Precoated Electrode. The formation of a polymer coating via reactions 1−3 alone cannot explain some of its properties observed in our previous study.[13] Its yellow color and reduced solubility in common organic solvents suggest that side reactions such as polymer branching and cross-linking may be occurring as well. Obviously, such processes can take place only after the polymer has been formed. To study the electrode reactions more extensively while the evolution of hydrogen at the cathode is minimized, we first precoated a mild steel electrode with poly(2-vinylpyridine) using a modified chronoamperometric method described previously.[13] The thickness of the coating so formed was estimated to be on the order of 10 μm. (Although not included here, we have shown that the electrochemical behavior on a mild steel electrode was qualitatively the same as that on a copper electrode.[38] Thus, the results from the SERS experiments with copper should be applicable to those from the CV experiments with mild steel in this section.) This coated electrode was then immersed in a 0.25 M 2-vinylpyridine solution at pH 4.8, and the voltammogram shown in Figure 5 was obtained. The voltammogram differs significantly from that observed for an initially bare metal electrode in several respects. First, it is possible for the potential scan to be extended as far as −2.5 V without severe hydrogen evolution occurring. Hydrogen evolution had begun to occur at approximately −1.5 V when the electrode was not precoated.[13] This widens the range of voltages over which reductive polymerization can be studied.

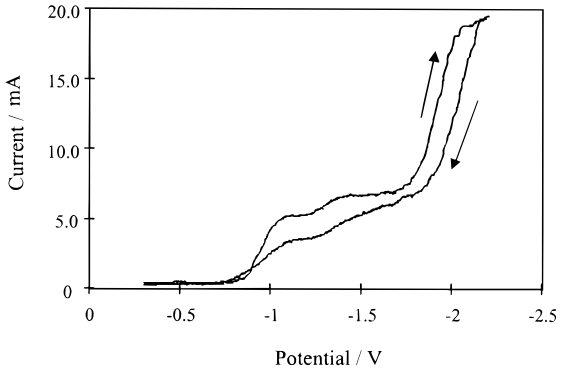


Figure 5. Cyclic voltammogram obtained on a precoated mild steel electrode immersed in an aqueous solution containing 0.25 M 2-vinylpyridine, 20 vol % methanol and 0.05 M NH_4ClO_4 at pH 4.8 adjusted with concentrated $HClO_4$. Potential scan rate = 30 mV/s. The three observed half-wave potentials are −0.95, −1.30, and −1.91 V, respectively. The arrows indicate the direction of the cycle.

A second important difference in the voltammogram in Figure 5 is the appearance of three current plateaus at half-wave potentials ($E_{1/2}$) of −0.95, −1.3, and −1.91 V before the very large current rise for extensive hydrogen evolution, indicating that more than one electrochemical reaction is occurring at the electrode. Although not shown here, we have obtained similar results with other electrode materials (e.g., zinc and lead) and other inorganic electrolytes (e.g., SO_4^{2-}, NO_3^-, Cl^-, and PO_4^{3-}).

To determine the origin of these current plateaus, the following experiment was conducted. Poly(2-vinylpyridine) formed by a free radical bulk polymerization process was dissolved to form a 0.1 wt % aqueous polyelectrolyte solution. The other components of the solution (the methanol content, the type and concentration of inorganic salt, etc.) were maintained the same as used for electropolymerization, except that no 2-vinylpyridine monomer was added. The solution pH was adjusted using $HClO_4$ and NH_4OH, but could only be adjusted to a stable value lower than 2.9 or higher than 9.2. A mild steel electrode precoated with poly(2-vinylpyridine) was used as the working electrode. The voltammogram at pH 2.9 (Figure 6a) clearly shows two current waves before the hydrogen evolution rise. However, the plateau with $E_{1/2}$ of −0.95 V in Figure 5 does not appear in Figure 6a. Since Figure 6a has been obtained in a solution that does not contain any 2-vinylpyridine monomer, this suggests that the wave with $E_{1/2}$ of −0.95 V can be attributed to the reduction of the monomer. This result is also consistent with the $E_{1/2}$ for 2-vinylpyridine reduction reported in the literature.[39] The $E_{1/2}$ of −1.24 and −1.88 V for the two plateaus in Figure 6a are very similar to those of the second and third plateaus in Figure 5, suggesting that they can be attributed to the same processes. These presumably involve reduction reactions in which dissolved polymer is participating.

Although one must be careful in relating these CV results to the SERS spectra in the previous section, since the latter were obtained on initially bare metal electrodes, it is important for our interpretation of the

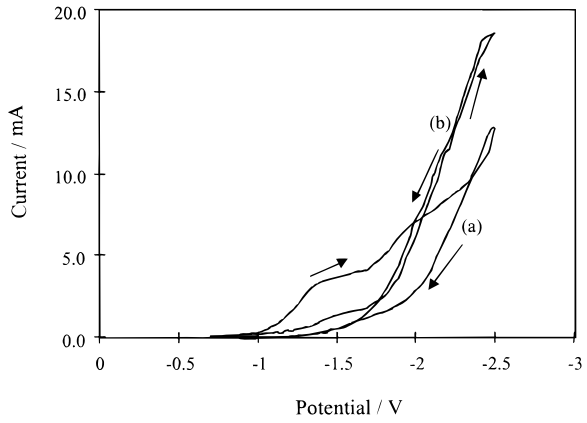


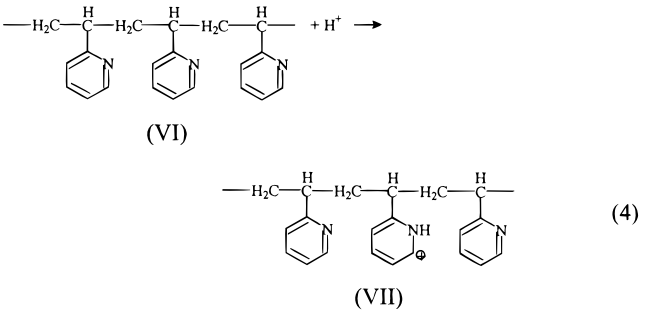
Figure 6. Cyclic voltammogram obtained on a precoated mild steel electrode immersed in an aqueous solution containing 0.01 M poly(2-vinylpyridine) polyelectrolyte, 20 vol % methanol, and 0.05 M NH_4ClO_4 at (a) pH 2.9, adjusted with concentrated $HClO_4$ and (b) pH 9.2, adjusted with concentrated NH_4OH. Potential scan rate = 30 mV/s. The poly(2-vinylpyridine) was formed by a bulk polymerization process, with 0.1 wt % benzoyl peroxide as initiator. The two observed half-wave potentials are −1.24 and −1.88 V, respectively. The arrows indicate the direction of the cycles.

reaction mechanism that they are consistent regarding the first plateau in Figure 5. The SERS results indicated that, by potentials of at least −0.3 V, significant changes proposed by us to include reactions 1−3 have begun to occur on the electrode surface. Although the three reaction steps would be required for monomer reduction, only the third one would lead directly to the current flow in the first plateau in Figure 5. There is not necessarily a problem associated with attributing the changes beginning at −0.3 V to the first plateau in the CV to the same process, since the onset of current flow would occur at the foot of the plateau, which obviously must be more positive than −0.95 V. In general, it is difficult to determine from any CV precisely where the current would begin to rise. Also, SERS is particularly sensitive to pyridine-based species which are strongly Raman-active.

When the pH is increased to 9.2, the resulting CV on the precoated electrode (Figure 6b) appears very similar to one obtained in a previous study[13] on a precoated mild steel electrode without any 2-vinylpyridine monomer or poly(2-vinylpyridine) polymer dissolved in solution.

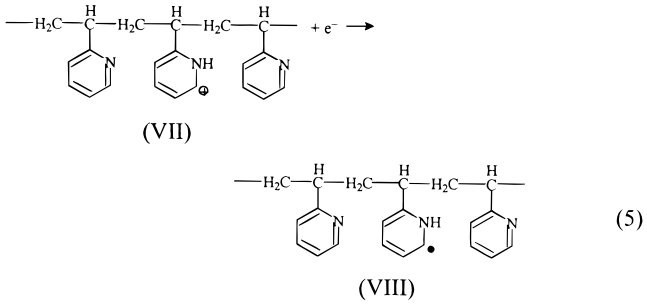
It is also similar to CVs obtained on bare metal electrodes in 0.25 M 2-vinylpyridine when no polymer coating is observed to form. This suggests that H_2 evolution is the only process occurring on the precoated electrode at this pH.

One possible explanation for the appearance of the two plateaus with $E_{1/2}$ of −1.3 and −1.91 V is that the polymer chain itself is undergoing electrolytic reduction. A mechanism involving more than one electron-transfer reaction is more complex than the conventional single-electron-transfer mechanism proposed for electropolymerization.[40,41] However, this is not the first time that electrolytic reduction of a polymer chain has been proposed. Similar phenomena have been reported recently for the in situ electropolymerization of maleic anhydride in an acetonitrile−dimethylformamide mixture [42] and of allylphenyl ether in acetonitrile[43] and for the adsorption of dissolved poly(2-vinylpyridine) from aqueous solution.[44] The effect can be attributed to the ionization of the polymers after they are produced. In our case, poly(2-vinylpyridine) is a weak base with a pK_a value of about 4[45] that could be protonated in the acidic solution as follows:[44,46,47]



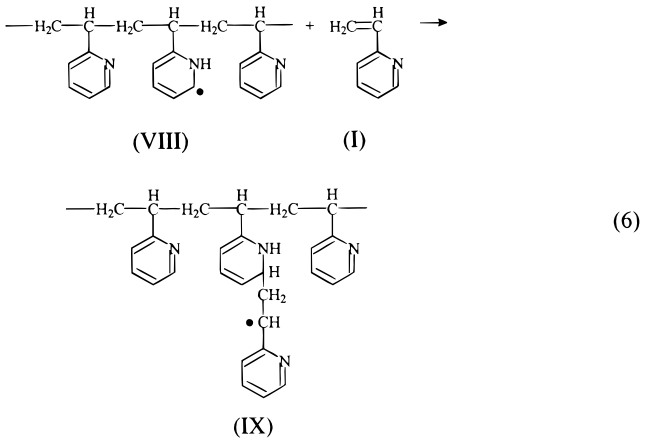
(4)

The protonated polymer chain (VII) could then be attracted to, and undergo reduction at, the cathode surface. In addition, polymer chains attached to the cathode can be similarly protonated. The occurrence of such a mechanism in a number of systems has been summarized by Hillman.[3] This provides a means by which inactive polymer chains (VI) become reactivated (VIII). Therefore, when a poly(2-vinylpyridine) coating is formed at the electrode surface, it may involve not only reduction of protonated 2-vinylpyridine monomer but also reduction of the protonated polymer that has already been produced:



(5)

These pendant radicals (VIII) could then propagate with neutral monomer to form activated polymer chains with a highly branched and cross-linked structure:



(6)

These polymers can be further protonated and reduced at the cathodic surface, making the polymer even more branched and cross-linked. This could explain the fact that the solubility of these poly(2-vinylpyridine) coatings in organic solvents is less than that of the polymer formed by bulk polymerization.[11−13]

Poly(2-vinylpyridine) coatings produced by electropolymerization have been consistently found by us[13] and

others[11,12] to be yellow in color rather than colorless, as is the case for the polymer formed by bulk polymerization of the monomer. A similar effect has been observed in the formation of other polymer coatings by electropolymerization. For example, Akbulut and Hacioglu [42] obtained a brown polymer coating on a platinum cathode surface from the colorless maleic anhydride. In our case, the polymerization is being initiated at a cathode surface, so other reduction reactions may affect the electropolymerization. For example, atomic hydrogen radicals are generated at the cathode surface and may combine with the polymer radicals and terminate the polymerization. Frequent chain termination by hydrogen or chain transfer to the monomer present may lead to a polymer product with a short chain length. At the same time, the inactive polymer chains may be protonated and reactivated by the mechanism described above. Ultimately, a polymer coating with a linearly short but highly branched and cross-linked network structure (as in IX) can be developed. Considering the fact that 2-vinylpyridine oligomers have been reported to have a yellow color,[11,12] the yellow color of the poly(2-vinylpyridine) coatings may be attributed to such a structure.

Finally, it is worthwhile to emphasize that the structures shown for the pyridinium ion (II and III), monomeric free radical (V), charged polymer chain (VII), and polymeric radicals (VIII and IX) are not necessarily the only possible forms. They are among the possible canonical forms caused by the delocalization of the positive charge on the nitrogen atom in the pyridine ring. The appearance of more than one reduction wave during the potential scan in Figure 5 could presumably reflect the fact that reduction occurs at different types of sites during this branching and cross-linking process. However, it is impossible for us to predict the exact structure of the polymer at this stage. We carried out a molecular structure study using ^{1}H NMR spectroscopy, but this provided inconclusive results due to the overlap of the absorptions of the methine protons with those of the methylene protons in poly(2-vinylpyridine).[48,49] Also, as discussed by us[28] and others,[12] the average molecular weight and polydispersity of the polymer coating could not be determined since it was not possible to dissolve the coatings completely with solvents used for gel permeation chromatography. This may reflect the branched and cross-linked nature of the polymer coating structure.

Conclusions

On the basis of these experimental results, the following mechanism is proposed. In acidic solution, 2-vinylpyridine molecules are protonated and adsorb on the surfaces of the cathode. The adsorbed 2-vinylpyridinium ions are then reduced by an electron transfer reaction to free radicals that initiate the polymerization by combining with neutral 2-vinylpyridine molecules. The polymer chains formed remain relatively short due to the frequent occurrence of reactions such as hydrogen termination on the cathode surface and chain transfer. The polymer formed can be further protonated at its nitrogen sites, adsorbed on the cathodic surface, and reduced at more negative potentials (<-1.5 V) to form polymeric radicals. In this way, inactive polymer chains are reactivated to form highly branched and cross-linked poly(2-vinylpyridine) coatings on the electrode. The formation of polymeric chains that are short, but highly branched and cross-linked, would explain the yellow color and low solubility of the poly(2-vinylpyridine) coatings.

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