Proton Uptake by Poly(2-vinylpyridine) Coatings

NISIT TANTAVICHET, MARK D. PRITZKER, CHARLES M. BURNS

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

ABSTRACT: A titration technique has been used to directly measure the proton uptake by ion-exchange poly(2-vinylpyridine) coatings as a function of solution pH. Contrary to the common assumption that each nitrogen in the pyridine ring is attached to an H^+ when the polymer film is fully protonated, the use of the titration technique has shown that the portion of the pyridine sites actually protonated does not exceed 25% anywhere in the pH range where the coating is stable. The pK_a value for the poly(2-vinylpyridine) coating has also been estimated to be 4.5 from the titration curve. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1493–1497, 2001

Key words: proton uptake; electropolymerized coatings; poly(2-vinylpyridine); titration

INTRODUCTION

Ion-exchange polymer-modified electrodes consist of thin films of electroactive polymers in which the redox-active species are electrostatically bound. In contrast to fixed-site redox polymers in which the polymer is formed and redox-active sites are incorporated in the same step, the preparation of ion-exchange polymers involves separate steps in which the polymer is first formed and then the redox-active groups are incorporated. The polymer structures are usually protonated or quaternized to permit electrostatic binding of anionic metal complexes (such as, $Fe(CN)_6^{3-/4-}$) or deprotonated to permit incorporation of cationic complexes (such as, $Ru(NH_3)_6^{3+/2+}$).

Because the capacity of these ion-exchange polymers is ultimately determined by the density of charged sites, it is important to determine the extent of protonation, quaternization, or deprotonation. For the most part, this has not been mea-

sured directly and instead has been estimated indirectly on the basis of the stoichiometry of the monomer and/or an elemental analysis of the polymer.

Important ion-exchange polymers include those based on poly(vinylpyridine). Poly(vinylpyridine) possesses electronegative nitrogen atoms in the pyridine rings that can be protonated in the presence of an acid to form polycationic polymer films. Anions in the electrolyte can then bind electrostatically to these protonated sites. To date, no work has been reported on the direct determination of the number of protonated sites in poly(vinylpyridine) films. Oyama and co-workers[1–3] adopted an indirect approach based on measurement of the average molecular weight of poly(4-vinylpyridine). They used this value together with knowledge of the structure of the monomer to estimate the number of pyridine sites. With the assumption that each nitrogen in the pyridine ring is attached to an H^+ ion when the polymer film is fully protonated, the number of protons incorporated into the film is equivalent to the number of pyridine sites. This method, however, can be inaccurate for a number of reasons. For one thing, this approach is only valid when the pyridine sites are fully protonated and so cannot

Correspondence to: M.D. Pritzker (Telephone: 519-888-4567, ext. 2542; Fax: 519-746-4979; E-mail: pritzker@cape.uwaterloo.ca)

yield the density of charged sites when the film is partially protonated. For another thing, it is possible that all the pyridine sites may not be accessible for protonation even under the most favorable solution conditions, particularly in the situation in which the film has been formed by electropolymerization. Recent studies[4–7] have shown that poly(2-vinylpyridine) coatings formed by electropolymerization are hard, compact, relatively insoluble, and nonporous, which may reflect a considerable amount of branching and crosslinking of the polymer structure. Finally, the method relies on the stoichiometry of the polymer being the same as that of the monomer. Thus, it is not applicable, for example, when the coating consists of a copolymer or when the coating has been chemically modified after polymerization.

It will therefore be preferable to base the determination of the density of charged sites on the direct measurement of the uptake of H^+ ions. Toward this end, we present a simple titration method to determine the amount of the protonated sites in poly(2-vinylpyridine) films. Protonation requires both the absorption of H^+ ions into the polymer film and their subsequent attachment to the pyridine ring. It is important to note that this method is not without some approximation. The uptake of H^+ ions into the film does not guarantee that all the protons will be electrostatically bound to the polymer matrix, particularly if the film is quite porous. This titration method cannot distinguish between bound and unbound protons in the film. Nevertheless, it is an improvement over the usual method that has been used. It should also be noted that the titration method has already been commonly used to characterize polymers; for example, determination of pK values.[8] However, to the authors' knowledge, it has not been applied to determine the extent of protonation in polymer coatings. The objective of this communication is to provide an example of its use and to compare the results to what would otherwise be obtained using the more common indirect method.

EXPERIMENTAL

The titration method was applied to poly(2-vinylpyridine) coatings formed by electropolymerization according to a procedure described previously.[5,9] The poly(2-vinylpyridine) was coated onto a cylindrical graphite electrode with an active area of 4.67 cm^2. The mass of polymer film

formed was ~4.7 mg, corresponding to a thickness of 11.1 μm (based on a polymer density of 0.9 g cm^{-3}). Once the coating was formed, it was placed in 100 mL of a 0.5 M KCl solution. The initial solution pH was measured with a pH meter (Orion Research Incorporated, Model 420A) and found to be typically ~5.5 before titration. Each titration step involved the addition of a small amount of HCl prepared from a standard solution (Sigma-Aldrich) followed by monitoring of solution pH until it reached a steady-state condition (~10–15 min at 25 °C).

During the experiment, the H^+ ion from the HCl in the bulk solution was absorbed into the polymer film, resulting in a protonated poly(2-vinylpyridine) film. The amount of H^+ absorbed into the polymer film was calculated from the mass balance of H^+ ion in the bulk solution before and after adding the fixed amount of HCl. The titration was carried out in a particular way to ensure that reliable results were obtained. We found that if HCl was successively added in small increments to a solution containing the same coating, the proton uptake measurement became increasingly unreliable as the pH was lowered. Presumably, the change in pH on absorption was becoming progressively smaller due to the logarithmic nature of the pH scale and the fact that the saturation capacity of the coating was being approached. Consequently, the limitations of the use of the pH meter to determine proton uptake became very important. This problem was also exacerbated by the fact that the mass balance calculation for each point on the titration curve was affected by the mass balances for all of the preceding points during the titration. As a result, the measurement errors tended to build up with each successive point.

For these reasons, the following approach was used to measure proton uptake during this study. Each point on the titration curve was obtained through a separate experiment in which a different amount of HCl was added to a KCl solution containing a new electrode with a freshly formed coating. An advantage of this approach was the initial pH for each uptake measurement was 5.5, so that substantial changes in pH on absorption were always being measured. Furthermore, because only a single titration step was carried out on a given coating during each experiment, the measurement error from point to point on the titration curve was not cumulative.

It should be acknowledged that, in addition to its time-consuming nature, a drawback to this

approach is the requirement that all freshly formed coatings used to construct the titration curve be similar enough that their proton uptake follow the same behavior. Our previous experience with the electropolymerization of poly(2-vinylpyridine)[5,9] has shown that the method for film formation used in this study leads to very reproducible polymer coatings. Moreover, as will be shown, the uptake measurements obtained on the different coatings produced a very smooth titration curve.

We also recognize that the use of a pH meter to measure proton uptake can become unreliable when the pH becomes low. However, this problem should not be significant in this study because the titration was continued only down to a pH of 3.0. The reduction of the pH to much lower values caused the polymer coatings to become unstable and therefore was not of interest.

The mass balance calculations to determine proton uptake require knowledge of the H^+ concentration rather than the measured pH. A series of blank titration experiments was therefore run to relate the measured pH to the corresponding H^+ concentration. These experiments were carried out in the same solution, using the identical procedure to that just described, except without the polymer coating present. Under such conditions, there should be no loss of H^+ from the solution due to absorption or chemical reaction. At the initial pH of 5.5 during each titration, virtually all carbonate dissolved in solution will already be in the form of CO_2 and therefore will not react with H^+ ions during the blank titration. Consequently, all the H^+ ions added to the solution during each titration with HCl should remain in solution. Thus, for each addition of HCl, the H^+ concentration and the corresponding measured pH (after equilibrium is reached) will be known and their correlation determined.

RESULTS AND DISCUSSION

The amount of H^+ absorbed is determined from the difference in the amount of H^+ in solution before and after adding HCl and is calculated from the following mass balance:

$$V_0(C_{H^+})_0 + V_{add}(C_{H^+})_{add} = V_1(C_{H^+})_1 + M_{ab} \quad (1)$$

where V_0 and $(C_{H^+})_0$ are, respectively, the volume (dm^3) and H^+ concentration $(mol\ dm^{-3})$ in the
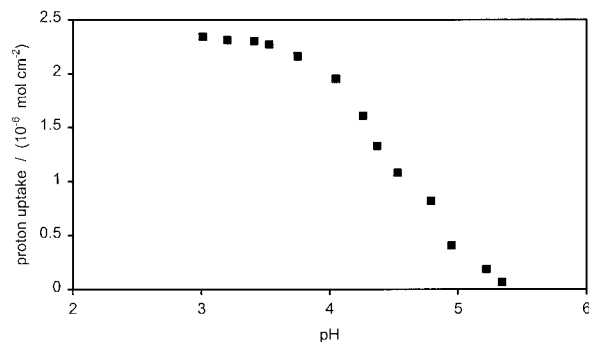

Figure 1 The effect of pH on the uptake Γ_{H+} of H^+ ions in poly(2-vinylpyridine) films immersed in 0.5 mol dm^{-3} KCl solutions.

KCl solution before the titration of HCl; V_{add} and $(C_{H^+})_{add}$ are, respectively, the volume (dm^3) and H^+ concentration $(mol\ dm^{-3})$ of the standard HCl titrant solution; V_1 and $(C_{H^+})_1$ are, respectively, the total volume and H^+ concentration after the titration; and M_{ab} is the total amount of H^+ absorbed in the polymer film (mol). $(C_{H^+})_0$ and $(C_{H^+})_1$ are obtained by combining the pH measurements before and after HCl is added to the KCl solution with the pH–C_{H^+} correlation obtained from the blank titration experiments. The absorption density $(mol\ cm^{-2})$ of H^+ in the polymer film, Γ_{H^+}, can be defined as:

$$\Gamma_{H^+} = M_{ab}/A \quad (2)$$

where A is the electrode area exposed to the solution (cm^2).

The resulting titration curve showing Γ_{H+} plotted versus the equilibrium pH is shown in Figure 1. The x coordinate for each point on the curve corresponds to the pH measured at the end of each titration when equilibrium is reached. The value of Γ_{H+} corresponding to this pH is calculated from the mass balance eqs. 1 and 2.

It should be noted that the proton uptake is dependent on the degree of swelling of polymer coatings. A previous study[9] has shown that the internal structure of poly(2-vinylpyridine) coatings is strongly influenced by the nature of the electrolyte in which it is immersed. For example, poly(2-vinylpyridine) coatings become more rigid and compact in solutions containing ClO_4^- than in those containing other anions such as Cl^-, NO_3^-, Br^-, and SO_4^{2-} because ClO_4^- promotes dehydration, crosslinking, and branching[10,11] with the polymer matrix. In this study, poly(2-vinylpyridine) coatings were immersed only in KCl solu-

tions under relatively mild conditions (pH 3–5.5). Consequently, the poly(2-vinylpyridine) structure was open enough to allow protonation, but not enough to become unstable. It should be noted that the coatings still remained quite firm, with no evidence of being gel-like at the lowest pH of 3.0. Preliminary experiments were carried out to determine the length of time required for the pH to stabilize after each addition of HCl. A period of only 20 min was needed at room temperature.

As the equilibrium pH decreases from its natural condition, the number of protonated sites in the polymer film steeply increases before leveling off toward a plateau as the pH decreases to 3.0 (see Figure 1). The onset of a plateau indicates that the polymer film is becoming saturated with H^+ attached to the pyridine ring. The results show that the maximum density of protonated sites in the polymer films is 2.34×10^{-6} mol cm^{-2} when the pH is at its lowest value of 3.0. This titration curve is similar in shape to a result obtained in previous work in which a coating was immersed in a solution containing $Fe(CN)_6^{3-}$.[9] The amount of $Fe(CN)_6^{3-}$ incorporated into the polymer films also showed a similar very strong dependence on pH.

Based on the weight of the coating used in each titration experiment and the molecular weight of the 2-vinylpyridine monomer, the number of pyridine sites in the coating is estimated to be 9.57×10^{-6} mol cm^{-2} assuming the stoichiometries of the polymer and monomer are the same. With this value and the maximum density of protonated sites determined from titration, it is determined that the fraction of total pyridine sites that are actually protonated over the useful pH range of the coating does not exceed 25%. Thus, a common assumption that one H^+ attaches for every monomer unit does not hold in the case of this polymer coating. A finding that < 25% of the available sites are actually protonated is consistent with results from previous experiments conducted on the poly(2-vinylpyridine) coatings formed by electropolymerization.[4,7] These results provide strong evidence that the electropolymerization leads to a structure with a significant amount of branching and/or cross-linking. In such a structure, many of the pyridine rings may be inaccessible to H^+ ions from the bulk solution. This inaccessibility may explain a finding from a previous study that the coatings formed by electropolymerization have considerably higher chemical and corrosion resistance than those formed by dip coating using a solution of bulk polymerized 2-vinylpyridine.[9] Whereas the
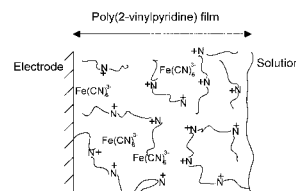

Figure 2 Schematic depiction of the electrostatic incorporation of $Fe(CN)_6^{3-}$ into a protonated poly(2-vinylpyridine) film on an electrode. N^+ is the protonated site corresponding to the nitrogen in the pyridine group.

dip-coated films were no longer stable and peeled from the graphite surface when the pH was lowered to 3.0, the electropolymerized coatings still remained intact.

The titration curve also allows estimation of the pK_a value of the electropolymerized poly(2-vinylpyridine). This parameter can be approximated as the pH at which the proton uptake reaches 50% of its maximum level. Strictly speaking, this estimation is applicable only when the uptake has leveled off completely to a plateau and become saturated. Although the proton uptake in Figure 1 may not have reached an absolute maximum when a pH of 3.0 is reached, it is close enough that a good estimate of pK_a can be made. This value is ~4.5 according to the titration curve in Figure 1. Very little has been reported in the literature concerning the pK_a value of poly(2-vinylpyridine). Ferruti and Barbucci[12] reported values in the range 3.25–3.95 for dissolved poly(2-vinylpyridine) in 45 weight % ethanol solutions depending on the ionic strength (i.e., varying NaCl concentration). Although the pK_a value of poly(4-vinylpyridine) would be expected to differ from that of poly(2-vinylpyridine), the comparison is still worth noting. Chanda et al.[13] obtained a value of 5.8 for commercial, solid, cross-linked poly(4-vinylpyridine). Because protonation of partially charged poly(2-vinylpyridine) is more difficult that that of poly(4-vinylpyridine) of the same charge density, one would expect the former to have a lower pK_a value. The value of 4.5 for the poly(2-vinylpyridine) coatings obtained in this study is consistent with this expectation.

From our previous work,[9] the maximum amount of $Fe(CN)_6^{3-}$ confined in the films in the pH range corresponding to the plateau was determined to be 4.4×10^{-7} mol cm^{-2}, which corresponds to ~19% of the maximum measured proton uptake.

Theoretically, each $Fe(CN)_6^{3-}$ molecule should be bound to three protonated sites of the polymer

structure, as sketched in Figure 2. Thus, the maximum amount of $Fe(CN)_6^{3-}$ that can be incorporated into the film should correspond to 33% of the total number of protonated sites. This assumes that the $Fe(CN)_6^{3-}$ has entirely displaced the exchangeable anion initially present in the film. The value estimated from the titration technique seems reasonable because it is close to, but does not exceed this level. Oyama and co-workers reported the number of $Fe(CN)_6^{3-}$, $IrCl_6^{3-}$, and $Mo(CN)_8^{4-}$ ions incorporated into poly(4-vinylpyridine) films to correspond to ~40%,[1] 40%,[2] and 30%[3] of the total number of pyridine sites, respectively.

CONCLUSIONS

A titration technique has been used to obtain information on the uptake of protons in the polymer film as a function of solution pH as well as on the relative amounts of $Fe(CN)_6^{3-}$ and H^+ that are absorbed into the film. On the basis of the polymer coating weight and the density of protonated sites determined by this titration method, the fraction of pyridine sites that are protonated has been found to never exceed 25%. The pK_a value of electropolymerized poly(2-vinylpyridine) film has also been determined using information from the titration curve. When the polymer film is fully protonated, the maximum uptake of $Fe(CN)_6^{3-}$ corresponds to 19% of the amount of H^+ absorbed by the film.

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