In Situ UV–Vis Spectroelectrochemical Study of Polyaniline Degradation

ALBERTAS MALINAUSKAS,* RUDOLF HOLZE

Technische Universität Chemnitz, Institut für Chemie, D-09107 Chemnitz, Germany

ABSTRACT: The degradation of polyaniline at anodic potentials was studied with *in situ* UV–Vis spectroscopy of polymer-coated ITO glass electrodes. Spectral changes at high potential values were observed and discussed. Degradation follows first-order kinetics, with rate constants ranging from 8.40×10^{-6} to 2.93×10^{-3} s^{-1} at electrode potentials of $E_{\mathrm{NHE}} = +0.85$ to $+1.20$ V. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 287–294, 1999

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INTRODUCTION

Polyaniline (PANI) is known to be one of the most stable conducting polymers. However, degradation processes of PANI are known to proceed under a variety of experimental conditions. A number of articles have examined this phenomenon.

Kobayashi et al. showed, in their early works, that the two well-known peaks in cyclic voltammograms of PANI diminish in height during prolonged potential cycling, and a third redox process in the middle potential region becomes evident with increasing intensity.[1,2] These authors stated that the diminishing main peaks reflect the degradation of PANI; whereas, the middle peak is associated with degradation products. If the electrode potential is not swept beyond ca. $E_{\mathrm{SCE}} = 0.7$ V during potential cycling, no degradation is observed.

The nature of the peak in the middle potential region has been widely discussed. Based upon their voltammetric and spectroscopic studies,

Kobayashi et al. presented a reaction scheme for oxidative degradation.[2] In accordance with this scheme, p-benzoquinone was claimed as a resulting product of degradation. Stilwell and Park concluded that the peak in the middle potential region corresponds to redox reactions of degradation products of PANI, including p-benzoquinone and quinoneimines.[3–5] Yang and Bard showed p-benzoquinone and p-aminophenol to be responsible for the occurrence of the middle peak in the electropolymerization of aniline.[6] P-benzoquinone was also suggested elsewhere as degradation product,[7] it was identified with *in situ* IR spectroscopy by Neugebauer et al.[8]

On the other hand, Glarum and Marshall could not confirm formation of p-benzoquinone during overoxidation of PANI.[9] Cleavage of polymer chains as well as the linkage of neighboring chains were suggested as reactions occurring during oxidative degradation of PANI.[10–12] As an alternative, Genies et al.[13,14] proposed a different phenazine-like structure of PANI, formed at higher anodic potential and responsible for the occurrence of the middle peak. A detailed review on the degradation of PANI has been presented by Pud.[15]

In addition to electrochemical degradation of PANI, Pasquali et al. studied degradation processes of PANI and its derivatives in aqueous and

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organic solutions at open electric circuit and in the dry state.[16] In all cases, different degrees of degradation were observed.

The purpose of the work reported here was to study with *in situ* spectroelectrochemistry degradation kinetics of PANI in acid aqueous solution as a function of the applied electrode potential.

EXPERIMENTAL

Freshly distilled analytical grade aniline (Riedel-de-Haen) was used. All solutions were prepared with 0.5 M sulphuric acid, prepared from 18 mΩ water (Seralpur Pro 90 C).

UV-Vis spectra were recorded with a Shimadzu model UV-2101PC spectrometer. Spectroelectrochemical experiments were done in a 1-cm path length quartz cuvette with an indium-doped tin oxide (ITO)-coated glass electrode with a specific surface conductivity of ca. 10 Ω/square, installed perpendicular to the light path. A platinum wire was used as counter electrode; a relative hydrogen reference electrode was connected with the cell via a salt bridge. The reference electrode was filled with 0.5 m sulfuric acid solution. Before experiments, ITO glass working electrodes were degreased with acetone and rinsed with plenty of water. For every series of experiments, a new ITO glass electrode was used. In the reference channel of the spectrometer, a quartz cuvette filled with 0.5 m sulfuric acid solution containing an identical ITO glass electrode was placed.

PANI films were deposited potentiostatically at electrode potentials indicated in the text, comparability of film thickness was attempted by keeping deposition times constant. Because of the influence of the electrode potential on the rate of deposition, differences in the actual film thickness are possible. Potentiodynamic deposition was used in a few examples, films, in these cases, were certainly thinner, because the electrode potential was in a potential range sufficiently positive for electropolymerization for only a fraction of the total time.

A Wenking model LB 81 M potentiostat and Wenking MVS 87 voltage scanner (Bank Elektronik, Germany) were used. All potential values are reported with respect to the relative hydrogen electrode, filled with 0.5 m sulphuric acid.

RESULTS AND DISCUSSION

Figure 1, top, shows UV–Vis spectra of PANI film, deposited on ITO glass electrode at a controlled

Figure 1 Top: UV–Vis spectra of a PANI-modified ITO glass electrode in 0.5 m H$_2$SO$_4$ at different electrode potentials, ranging from E_{RHE} = 0.0 to +0.8 V recorded in intervals of 0.1 V. PANI-modified electrode was prepared by electropolymerization at E_{RHE} = 1.0 V in a solution of 0.5 m H$_2$SO$_4$ + 0.05 m aniline. Bottom: spectra of the same electrode, obtained after holding it at E_{RHE} = +1.0 V in 0.5 m H$_2$SO$_4$ for 10 min.

potential of +1.0 V, at various electrode potentials E_{RHE} = 0.0 to +0.8 V. Three characteristic absorbance bands can be seen. The band at λ = 315 nm correspond to the $\pi \rightarrow \pi^*$-transition of benzoid rings, characteristic for the leucoemeraldine form of PANI.[17,18] By shifting the electrode potential to higher values, this band diminishes in intensity, indicating a decreasing number of benzoid rings because of oxidation of the leucoemeraldine into the emeraldine form of PANI. A band at ca. λ = 430 nm shows an intensity maximum at E_{RHE} = +0.4 V. It corresponds to an intermediate redox state of the PANI film, which probably possesses nonconjugated benzoid rings in a polymer chain.[17–21] The main absorbance band in the red region of the UV–Vis spectra

Figure 2 Same as in Figure 1 for a PANI-modified electrode prepared at $E_{RHE} = +1.2$ V.

corresponds to the emeraldine state of PANI.[17–21] The intensity of this band increases progressively with the shift of electrode potentials to higher values, up to $E_{RHE} = +0.8$ V.

Figure 2, top, shows spectra of a PANI film electropolymerized at a higher potential of $E_{RHE} = +1.2$ V. The dependence of absorbance bands at $\lambda = 315$ nm and $\lambda = 430$ nm on the electrode potential is nearly the same as in case of the PANI film obtained at lower electropolymerization potentials (as in Fig. 1, top). However, significant changes are observed in the red region of the spectra. The main absorbance band of the emeraldine form observed at $E_{RHE} = +0.8$ V, becomes more flattened. Also, the maximum positions for the spectral bands in the potential region from $E_{RHE} = +0.1$ to $+0.4$ V are shifted into the NIR region, in contrast to the corresponding maxima located between 830 and 900 nm for PANI films obtained at lower polymerization potential. A band of the emeraldine form, located in the red region, appears less intense, as compared to the

band at $\lambda = 315$ nm of the leucoemeraldine form. For example, the absorbance ratio of the band at ca. $\lambda = 750$ nm, recorded at $E_{RHE} = +0.8$ V and the band at $\lambda = 315$ nm, recorded at $E_{RHE} = +0.1$ V decreases from 1.38 to 0.87 by changing the electropolymerization potential from $E_{RHE} = +1.0$ to $+1.2$ V.

Much flatter maxima in the red region are obtained for PANI films, electrodeposited by a potential cycling procedure (Fig. 3, top). Although an upper limit of $E_{RHE} = +1.2$ V was used in electropolymerization, the absorbance maxima are weaker (or consist of a few bands), as in case of PANI films, obtained at a constant controlled potential of $E_{RHE} = +1.2$ V (cf. top parts of Figs. 2 and 3).

Polyaniline is known to consist of polymer chains of various length, or degree of polymerization. This degree depends greatly on the applied electropolymerization conditions. As with chemical polymerization of aniline, polyanilines with

Figure 3 Same as in Figure 1 for a PANI-modified electrode prepared by potential cycling within the limits of $E_{RHE} = +0.1$ to $+1.2$ V at a scan rate of 50 mV/s.

average molecular weight ranging from 19,000 to 150,000 Daltons may be obtained by varying the preparation conditions.[22,23] The differences in absorbance bands in the red region of UV–Vis spectra observed for PANI films prepared by the use of various electropolymerization conditions (Figs. 1, 2, 3, top parts), indicate various forms of polymer to be formed, depending upon the conditions used. These forms may differ in degree of polymerization as well as in their structure and morphology. It may be concluded from these spectra, that PANI prepared at low anodic potentials (E_{RHE} = +1.0 V), has the most uniform structure, because the absorbance band of its emeraldine form has the most symmetric and pronounced narrow shape (Fig. 1). The bands observed for polymers prepared at higher polymerization potential are somewhat flattened, less symmetric, and obviously consist of several overlapping absorbance bands, indicating a presence of various polymer structures in the film. As a measure of polymer homogeneity in its emeraldine form, the ratio of absorbance at its red maximum (at ca. 750 nm) to the absorbance at 900 nm may be used. A high ratio A_{max}/A_{900} of ca. 1.87 for a PANI film prepared at the lowest polymerization potential used (E_{RHE} = +0.95 V) drops consecutively by extending the electropolymerization potential to higher values (Fig. 4). This is consistent with many earlier works on electropolymerization of aniline, where the presence of large amounts of degraded polymer was confirmed after application of high anodic potential limits during electropolymerization.[24] Unexpectedly less homogeneous polymer films are formed by the potential cycling procedure (A_{max}/A_{900} < 1, as in Fig. 3, top).

It is well known with conjugated chromophores, that the UV–Vis absorbance band shifts to longer wavelengths with a longer conjugated molecular chain.[25] Thus, it can be concluded from these data that more long-chain polymers are formed at higher electrode potentials used in electropolymerization. Consequently, a plot of the ratio A_{max}/A_{900} versus electropolymerization potential (Fig. 4) depicts the increase of the amount of high-molecular fraction in the resulting PANI film by the use of higher electrode potential during film preparation.

By holding the PANI-filmed electrode at high potentials in a solution without aniline, the degradation of PANI film proceeds. This results in diminished values of absorbance. The resulting spectra of anodically treated films of PANI, which were prepared under various conditions, are pre-

Figure 4   Dependence of the ratio of absorbance at band maximum position to absorbance at λ = 900 nm for PANI-modified electrodes on electropolymerization potential (hollow circles), and for the same electrodes, held additionally at E_{RHE} = +1.1 V in 0.5 m H_2SO_4 for 10 min (full circles).

sented in the bottom parts of Figs. 1, 2, and 3, respectively. The spectra of anodically treated PANI films look essentially similar to those of the parent films, although some differences can be noted. The height of the band in the red region at λ = 750 nm increases with the shift of electrode potential to higher values. However, a plot of relative absorbance versus electrode potential becomes less sloped for anodically treated PANI films, as compared to untreated ones (Fig. 5, top). Also, the maximum of the band around λ = 430 nm remains unchanged in position at E_{RHE} = +0.4 V. However, this maximum becomes more obtuse for anodically treated films (Fig. 5, bottom). The presence of several overlapping bands in the red region becomes more evident after anodic treatment, indicating the presence of different structures of polymer in the PANI film (cf. top and bottom parts of Figs. 1, 2, 3). An interesting feature of anodically treated PANI films is the faster decrease of absorbance at the red end of the spectrum than at the absorbance maximum (at ca. λ = 750 nm). As a result, the ratio A_{max}/A_{900} becomes somewhat greater for anodically treated films, especially for the films prepared at high anodic potentials (Fig. 4). It can be concluded, that the long-chain fraction of PANI is destroyed anodically to a relative greater extent, and, thus,

of electrode potential to higher values. Figure 6, bottom, depicts UV–Vis spectra of PANI-coated electrodes after applying an electrode potential of $E_{RHE} = +1.1$ V. A fast decrease of absorbance is evident from Figure 6, bottom, indicating a fast degradation of the PANI film. As compared to a spectrum obtained at a relatively low potential of $E_{RHE} = +0.8$ V (A in Fig. 6, bottom), a strong shift of absorbance maximum is observed after applying a high positive potential. This hypsochromic shift proceeds reversibly; that is, after moving back the electrode potential to the initial value of $E_{RHE} = +0.8$ V, the absorbance maximum returns almost to its initial position (cf. spectra A and B in Fig. 6, bottom). The hypsochromic shift depends greatly on the applied electrode poten-

Figure 5 Dependence of relative absorbance (A/A_{max}) on electrode potential for the absorbance band at $\lambda = 750$ nm (top) and at $\lambda = 420$ nm (bottom) with a PANI-modified electrode prepared at $E_{RHE} = +1.1$ V in 0.5 m H_2SO_4 + 0.05 m aniline (open circles), and for the same electrode, held at $E_{RHE} = +1.1$ V in 0.5 m H_2SO_4 for 10 min (filled circles).

the shortening of polymer chains causes the increased ratio A_{max}/A_{900} after an anodic treatment.

The decrease of absorbance at the maximum can be observed immediately during an anodic treatment of a PANI-filmed ITO glass electrode prepared at $E_{RHE} = +1.1$ V in 0.5 m H_2SO_4 + 0.05 m aniline in an electrolyte solution without aniline. Figure 6, top, shows the decrease of absorbance at various electrode potentials E_{RHE} = +0.85 to +0.95 V. It can be seen, that the rate of PANI film destruction increases with the shift

Figure 6 Top: change of absorbance at $\lambda = 720$ nm of a PANI-modified electrode prepared at $E_{RHE} = +1.1$ V in 0.5 m H_2SO_4 + 0.05 m aniline held in 0.5 m H_2SO_4 at various electrode potential values (as indicated). Bottom: UV–Vis spectra of a PANI-modified electrode obtained at $E_{RHE} = +1.1$ V in 0.5 m H_2SO_4 after various time periods (as indicated). A and B are spectra, obtained at $E_{RHE} = +0.8$ V before (A) and after the treatment at $E_{RHE} = +1.1$ V (B).

Figure 7 Dependence of absorbance maximum position in the red region (open circles) and absorbance value at its maximum position (filled circles) on applied electrode potential for a PANI-modified electrode obtained in 0.5 m H_2SO_4. The electrode was prepared by electropolymerization at $E_{RHE} = +1.1$ V in a solution of 0.5 m H_2SO_4 + 0.05 m aniline.

tial, especially at high potential values exceeding $E_{RHE} = +1.0$ V, where the pernigraniline form of PANI is most stable (Fig. 7). A large hypsochromic shift of ca. 200 nm, obtained after a shift of the electrode potential from $E_{RHE} = +0.80$ to $+1.20$ V results also in visible changes of the color of the PANI film from bluish green to purple at the highest potential values. A hypsochromic shift of the red absorbance band of PANI with increasing electrode potential has been observed previously. Recently, Brandl and Holze presented an explanation of this phenomenon, based on the assumption of a distribution of polymer chain segments of different effective conjugation lengths.[26] Based on this model, a decreasing average conjugation length of PANI chains is responsible for the hypsochromic shift observed after an anodic potential shift.

The kinetic data for the decrease of absorbance at its red maximum may be well linearized in first-order reaction coordinates; that is, ln A versus time. From the slope of these linearized data, a first-order decay rate constant can be calculated by the use of the following relationship:

$$k = -\Delta \ln A/\Delta t \qquad (1)$$

where k represents the rate constant, A the absorbance at its maximum position, and t time, respectively.

The calculated values of the rate constant, as well as of the half-time of PANI film degradation, are summarized in Table I. It is noteworthy, that in the entire potential range investigated ($E_{RHE} = +0.85$ to $+1.20$ V), the correlation coefficients for the linearized data exceeded 0.99, as calculated from seven experimental points for each potential value. The kinetic parameters depend greatly on the applied electrode potential and vary over several orders of magnitude. The half-time of film degradation ranges from ca. 23 h to ca. 4 min for the lowest and highest anodic potential used ($E_{RHE} = +0.85$ V and $+1.20$ V, respectively).

The dependence of the kinetic data, presented in Table I, on electrode potential, can be linearized according to the following relationship:

$$\log k = a + bE \qquad (2)$$

where a and b are empiric coefficients, and k and E are the first-order rate constant and electrode potential, respectively (see Fig. 8).

A linear regression analysis of the data yields: $a = -12.7$, $b = 8.96$ V^{-1}, and correlation coefficient $r = 0.993$ (from 6 points) in the electrode potential range of $E_{RHE} = +0.85$ to $+1.10$ V. The results show a linear dependence of log k on the electrode potential within more than two orders of magnitude for the degradation rate constant. A high slope of log k versus E (i.e., a large coefficient b) shows a high sensitivity of degradation rate on

Table I First-Order Rate Constants k/s^{-1} of PANI Film Degradation and Half-Time $t_{1/2}$/min of Degradation at Electrode Potentials Ranging from E_{RHE} +0.85 to +1.20 V

E_{RHE}/V	k/s^{-1}	$t_{1/2}$/min
0.85	8.40×10^{-6}	1375 (22.9 h)
0.90	1.40×10^{-5}	825 (13.8 h)
0.95	7.00×10^{-5}	165 (2.75 h)
1.00	1.82×10^{-4}	63.6 (1.06 h)
1.05	4.92×10^{-4}	23.5
1.10	1.12×10^{-3}	10.4
1.15	2.32×10^{-3}	4.5
1.20	2.93×10^{-3}	3.9

Figure 8 Dependence of logarithm of the first-order rate constant of electrochemical degradation a PANI film in 0.5 m H_2SO_4 on electrode potential. PANI-modified electrode was prepared at $E_{RHE} = +1.1$ V in 0.5 m $H_2SO_4 + 0.05$ m aniline.

electrode potential. In a formal sense, an increase of electrode potential by 1 V causes an increase of the degradation rate by ca. nine orders of magnitude.

CONCLUSIONS

Anodic degradation of PANI has been well known for more than 10 years. In past years, intense work on PANI degradation was stimulated by the possible application of this material in such fields as batteries or electrocatalytic systems. It is frequently accepted that almost no degradation of PANI and some of its derivatives occurs at low electrode potentials; for example, not exceeding $E_{SCE} = +0.6$ V.[27]

However, the results presented here show, that degradation proceeds to a significant extent at electrode potentials as low as $E_{RHE} = +0.85$ V. Pasquali et al. studied the degradation of PANI under a va-

riety of conditions, including open circuit situations. They found more or less extended degradation to proceed in almost all cases.[16] These authors painted a picture with unpleasant shadows concerning the stability of PANI and its potential applications. We can accept the results presented here as maintaining this pessimism. However, it may be also concluded from our results that, under certain conditions, the degradation can be minimized to a perhaps acceptable level. Thus, assuming a linear dependence of log k versus E (i.e., the same or very similar processes are taking place at lower electrode potentials), described by eq. (2) and depicted in Figure 8, to be valid for lower electrode potentials below the limits studied, we can easily calculate from eq. (2) a degradation rate constant at lower electrode potential values. For example, at an electrode potential of $E_{RHE} = +0.6$ V (i.e., a middle value between leucoemeraldine/emeraldine and emeraldine/pernigraniline transitions of PANI), a degradation rate constant of 4.7×10^{-8} s^{-1} may be obtained according to eq. (2), yielding a half-period of 170 days. Thus, satisfactory stability of PANI may be possible at lower electrode potentials.

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